S. Department of Commerce
Henry A. Wallace, Secretary
National Bureau of Standards
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Journal of Research of the National Bureau of Standards

SEPTEMBER 1946

VOLUME 37

NUMBER 3

UNITED STATES
GOVERNMENT PRINTING OFFICE
WASHINGTON : 1946

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S. Department of Commerce
tional Bureau of Standards

Research Paper RP1736
Volume 37, September 1946

Part of the Journal of Research of the National Bureau of Standards

ffect of Reaction Between Mercury and Oxygen Upon Polarographic Waves of Certain Metals at Small Concentrations

By *Edgar Reynolds Smith, John Keenan Taylor, and Roberta Evelyn Smith*

Polarographic waves of certain metals, notably of lead, zinc, copper, cobalt, and nickel in dilute neutral solutions, diminish progressively with time in the presence of mercury and air. This behavior is not to be explained by adsorption, as has previously been supposed, but by a reaction between mercury, water, oxygen, and the ions of the metallic salt which, in some instances, precipitates the metal from solution in the form of its hydroxide. This reaction is

$$2Hg+H_2O+1/2\ O_2+MCl_2=Hg_2Cl_2+M(OH)_2,$$

in which M represents the metal. Recognition of this reaction and precautions to exclude it are essential for accurate polarographic determinations of small amounts of heavy metals.

I. Introduction

The polarographic method has been used for the ermination of small amounts of metals in ores d alloys [1, 2, 3, 4],[1] plant ashes [5], biological terials [6], samples collected in industrial giene studies [7, 8], mineral waters [9], and other terials. Many references could be cited, but se suffice for typical examples. The presence an unsuspected systematic error in such deter-nations might lead to expensive mistakes in the e of an ore or the composition of an alloy, or ght cause unfortunate consequences through approval of unsafe respiratory equipment. example, if a polarographic analysis for the ount of lead in fumes were to give a negative lt when lead was actually present, serious m to the health of workers could result.

During the course of some work on the amount lead that might enter a cup of tea from certain zes, the polarographic waves produced by small concentrations of lead in neutral solutions were observed to decrease progressively to the point of extinction when the solutions were allowed to stand in contact with mercury and air. This behavior must have been found by others, since Kolthoff and Lingane [10], in their review of principles and applications of the polarographic method, say:

"Adsorption of electroreducible ions (particularly heavy-metal ions) by the glass wall of the cell must be prevented. Such adsorption may be particularly marked when dealing with very small

[1] Figures in brackets indicate literature references at the end of this paper.

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concentrations of heavy-metal ions (e. g. micropolarographic determination of lead ions), but it can usually be prevented by acidifying the solution."

However, an investigation of the matter has led us to conclude that the effect is not one of adsorption but instead is the result of a chemical reaction similar to the reaction

$$2Ag+2HCl+1/2\ O_2=2AgCl+H_2O,$$

which is known to disturb the potential of the silver–silver-chloride electrode [11, 12]. According to this analogy, the reaction that causes the heavy-metal ion to disappear from solution in the polarographic cell is

$$2Hg+H_2O+1/2\ O_2+MCl_2=Hg_2Cl_2+M(OH)_2,$$

in which M represents the heavy metal. The reaction probably occurs in the two stages

$$MCl_2+2H_2O=M(OH)_2+2HCl$$

and

$$2Hg+2HCl+1/2\ O_2=Hg_2Cl_2+H_2O,$$

the net result of which is expressed by eq 1.

The experimental work on which is based the conclusion that the effect is one of chemical action rather than adsorption is reported in the paper.

II. Experimental Details

Two polarographs of the photographic recording type were used. One of these was the model VIII instrument of V. & J. Nejedly, Prague, Czechoslovakia, described in a previous paper [13] and the other a Sargent-Heyrovsky model XII instrument. The electric measuring circuits of both were calibrated by measuring the potential drop across a standard resistor, which was substituted for the polarographic cell.

The dropping-mercury electrode used in most of the work was made by sealing a piece of capillary tubing of approximately 0.05-mm bore to a reservoir of large cross section so that no significant decrease in the driving head occurred during an operational period of about 1 hour. Periodic addition of mercury sufficed to maintain constant to better than 1 percent the mass-flow from the electrode. Frequent measurements of the drop-time and the mass-flow were taken to make sure that conditions were comparable during a series of measurements.

The cells were of the familiar Erlenmeyer type and provided for inert gas to flow through the solution before and over the solution during measurements, to exclude oxygen. The nitrogen used for this purpose was freed from oxygen by passage over copper heated to 450° C and then saturated with water vapor before introduction into the cell to minimize concentration errors arising from evaporation.

For the most part, stock solutions were made by dissolving in acid known quantities of the pure metal, evaporating to dryness, and diluting with water to a known volume. Where this was not feasible, salts of known purity were used. These stock solutions were diluted quantitatively to the concentration desired for a particular experiment. Sufficient quantities were prepared at any one time to provide for all the measurements of a particular series so that errors could not enter from differences in composition of the solutions. Maxima in the waves were suppressed by the addition of 0.01 percent of gelatin to the solution.

III. Results and Conclusions

If the effect were one of adsorption, repeated pipetting out and refilling the cell with fresh solution would finally establish the adsorption equilibrium between a solution of the original composition and the glass, and the wave height would then remain constant with time. To make this experiment, 3 ml of a solution containing 10^{-6} g of lead and 0.025 g of potassium chloride was allowed to stand over the pool of mercury in a polarographic cell. At intervals the air was displaced by nitrogen and a polarogram taken. Between these intervals air was allowed to diffuse into the solution. The lead wave progressively decreased and practically disappeared within 24 hours. The

ution was then pipetted out, fresh solution of original composition put in the cell, and the t repeated. After a number of such refillings lead wave continued to disappear just as idly as for the first filling, with no indication of supposed adsorption attaining an equilibrium. another experiment, a portion of solution of the ne composition was allowed to stand in contact h crushed Pyrex glass for 24 hours before intro- tion into the cell. The wave obtained for the d was then no different from that exhibited by ortion of the same solution which had not been contact with ground glass. If adsorption had urred, the lead wave would have been smaller. Portions of a solution containing about 7×10^{-6} f zinc and 13×10^{-6} g of cadmium per milliliter 0.1 *N* potassium chloride were put into three rex flasks. One flask was nearly filled with und Pyrex glass, one contained several milli- rs of mercury, and the other was clear. After nding in these flasks for 24 hours in contact h air, the solutions were poured into cells and arograms were made. The wave heights ained were as follows:

Flask	Height of wave	
	Cd	Zn
	mm	*mm*
Clear	25. 0	23. 6
Crushed glass	24. 2	23. 4
Mercury	21. 6	3. 0

Two portions of the same initial solution were ced in cells with pools of mercury for anodes d polarograms of the wave heights were taken. en air was bubbled through one of these for 5 rs, and nitrogen was bubbled through the r for 24 hours. Polarograms were taken, and n these it was found that the zinc wave had ctically disappeared in the former but had reased by only 8 percent in the latter. The dmium wave remained practically the same in h cells.

In all cases it was found that the original wave ghts were restored by the addition of a small ount of acid, which has the effect of preventing reversing the reaction expressed by eq 2. As g as acid is present hydrolysis does not occur, according to eq 3, hydrochloric acid is consumed by mercury and oxygen to form mercurous chloride and water. Thus, if oxygen is not excluded, in acidic solution the hydrogen wave must first decrease to extinction before hydrolysis begins to affect the wave of a metallic ion. A solution containing cadmium and zinc was acidified with hydrochloric acid so that the waves of hydrogen and of the two metals could be recorded consecutively on the same polarogram. The solution was exposed to air and polarograms were made at intervals. The hydrogen wave decreased progressively from an initial height of about 23 mm to complete disappearance after little more than 75 minutes. Meanwhile the waves of cadmium and zinc remained constant within experimental error. During this time the surface of the mercury became coated with a layer of calomel, which reduced the effective exposed area of the mercury. For this reason, the wave of zinc did not decrease very rapidly after the acid had disappeared. Air was then bubbled through the solution for 2 hours, and the wave of zinc decreased to 3.5 mm from an initial height of about 11 mm. The wave of cadmium remained unchanged. These results are summarized in table 1.

TABLE 1.—*Effect of oxygen when acid is present*

Time of exposure to air	Wave heights		
	H	Zn	Cd
Minutes	mm	mm	mm
0	22. 8	10. 4	10. 7
15	14. 6	11. 3	10. 5
45	8. 8	12. 5	10. 8
75	3. 0	10. 6	11. 0
195	0. 0	11. 4	10. 4
Air bubbled for 120 minutes more	.0	3. 5	10. 6

If the effect is caused by the chemical reactions represented by eq 1 and 2, the minimum height to which a wave decreases should depend upon the solubility of the hydroxide of the metal in question. Unfortunately, there are no data for the solubility of these heavy metal hydroxides in potassium chloride solutions and even such data as exist for pure water appear to be inconsistent and unreliable. Also, eq 1, 2, and 3 are intended to represent the principle of the effect involved and not the exact mechanism operating in every case. For example, the same principle gives an explanation of why the effect does not occur when the supporting electrolyte is potassium nitrate

instead of potassium chloride. For nitrate solutions, eq 3 becomes

$$2Hg+2HNO_3+1/2O_2=2HgNO_3+H_2O. \quad (4)$$

Mercurous nitrate in dilute solution, however, hydrolyzes to give a basic precipitate, $Hg_2(OH)NO_3$ and possibly some Hg_2O, with sufficient affinity to prevent the hydrolysis of zinc nitrate and the precipitation of zinc hydroxide. If a little solid mercurous nitrate is added to a saturated solution of zinc hydroxide in contact with excess solid zinc hydroxide, a large polarographic wave for zinc is actually obtained. The principle of this reaction is expressed by the equation,

$$Zn(OH)_2+2HgNO_3=Zn(NO_3)_2+Hg_2O+H_2O,$$

from which it is clear why the waves do not disappear in solutions of nitrates.

The behavior of several other metallic ions in neutral solutions of potassium chloride in the presence of air and mercury was also studied with results which are summarized in figure 1. Of these ions, thallium, manganese, and cadmium undergo little or no change even on prolonged contact. The waves for cobalt and copper, like those for zinc and lead, show rapid decreases, while the results for nickel are intermediate. The rate of decrease of a wave in any instance is, of course, dependent upon such factors as the area of the mercury surface, the amount of stirring, and the concentration of the ion. Under comparable conditions, the rates of decay are approximately in the order of the hydrolysis constants of the metallic ions, in further confirmation of the mechanism of chemical reaction rather than adsorption.

The rate of decrease of wave height for a given metallic ion depends markedly on its concentration. With concentrations of about 10^{-4} g/ml it was found that the lead and zinc waves decrease by only about 10 percent in 24 hours in contrast to the larger rates, shown in figure 1, for more dilute solutions of these ions. Errors of 10 to 20 percent have been noted in polarographic determinations of lead in neutral solutions when exposed to mercury for the short time necessary to expel oxygen from the solutions. Since the effect does not occur when the supporting electrolyte is acidic, it is safer to make polarographic measurements of dilute solutions of heavy metallic i in acidic rather than in neutral media when t anode is a pool of mercury. In cases where t reduction wave of hydrogen interferes and ac solutions cannot be used, it is possible to av the effect by preliminary elimination of oxyg from the solution before contact with mercu by the use of an external anode [14] or of a silv silver-chloride anode wound in spiral around dropping-mercury cathode [15], or with a cell the design devised by Lingane and Laitinen [

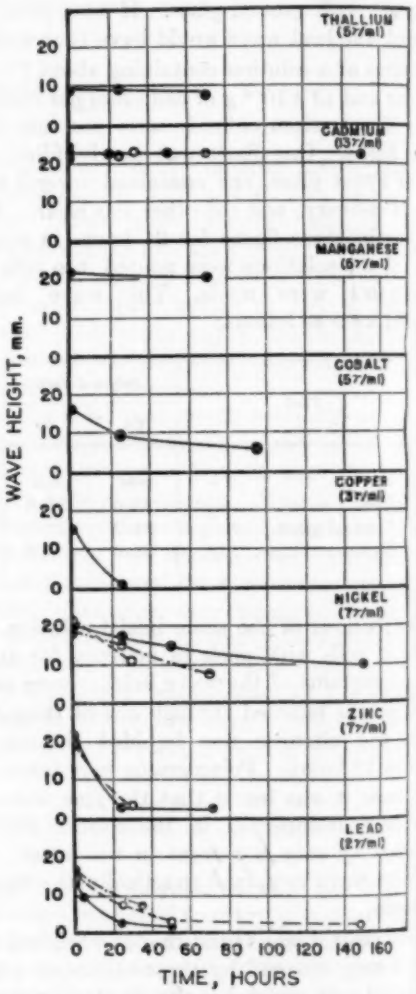

FIGURE 1.—*Changes in wave heights with time.*
The open and shaded circles represent different experiments.

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WASHINGTON, June 24, 1946.

S. Department of Commerce
ional Bureau of Standards

Research Paper RP1737
Volume 37, September 1946

Part of the Journal of Research of the National Bureau of Standards

heory for Axial Rigidity of Structural Members Having Ovaloid or Square Perforations

By Martin Greenspan

Formulas are derived for computing the over-all lengthening (or shortening) of a tension (or compression) member having a uniform gross cross section and a series of similar perforations of approximately ovaloid or approximately square shape uniformly distributed along the length.

I. Introduction

n a previous paper [1][1] the author demonted a method for computing the axial rigidity a tension or compression member having a form gross cross section and a series of similar forations of circular or elliptical shape uniy distributed along the length. The axialdity factor K is defined so that KEA_g is the dity that should be used in place of EA_g in the inary formula for computation of the extension the member. Here E is Young's modulus of sticity, and A_g is the gross cross-sectional area. e present paper extends this method to other pes of perforation, originally described in erence [2]. The boundary of the hole has the rametric equation

$$x=p\cos\beta+r\cos 3\beta,\ y=q\sin\beta-r\sin 3\beta. \quad (1)$$

Equation 1 represents a closed curve having metry about the x-axis and about the y-axis, which, for appropriate values of p, q, and r, s not cross itself. By adjustment of the lues of p, q, and r, a variety of curves is obtained, luding a good approximation to an ovaloid (a are with a semicircle erected on each of two posite sides) and a good approximation to a are with rounded corners, as well as exact ellipses ($r=0$) of any eccentricity. The approximate ovaloid obtained by taking

$$p=2.063,\ q=1.108,\ r=-0.079, \quad (2)$$

is shown compared to the actual ovaloid in figure 1. The approximate square obtained by taking

$$p=q=1,\ r=-0.14 \quad (3)$$

is shown in figure 2. The sides of the square are parallel to the axes of coordinates. By taking

$$p=q=1,\ r=0.14, \quad (4)$$

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[1] Numbers in brackets indicate literature references at the end of this paper.

the same square, but with the diagonals parallel to the axes of coordinates, is obtained. The radius of curvature at the midpoint of the fillet is about 0.086 times the length of the side of the square.

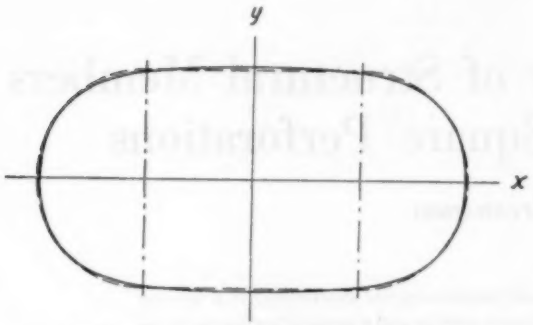

FIGURE 1.—*Actual and approximate ovaloids.*

The dashed line represents the actual ovaloid and the full line the approximate ovaloid of equations 1 and 2

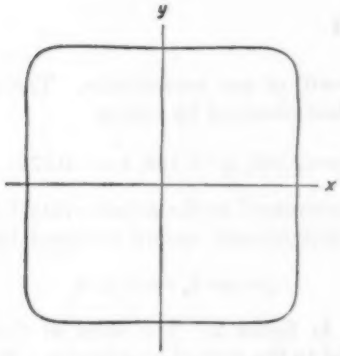

FIGURE 2.—*The approximate square of equations 1 and 3.*

It is shown in [1, eq 2][2] that for a member having perforations spaced $2l$ apart along the z-axis (parallel to the load), the axial rigidity factor K is given by

$$\frac{1}{K}=1+\frac{E}{Pl}\int u_x dydz,$$

in which u_x is the x-component of the displacement of the boundary of the hole, and the surface integral is extended over half the boundary of the perforation. The values of the load P and the displacement u_x may be assumed, for sufficiently large values of l and of A_z compared to the dimensions of the perforation, to be the same as in an infinite plate under uniform stress S_z disturbed by a single perforation.

For a member having circular holes, and gross cross-sectional area A_z and net cross-sectional area A_n,

$$P=S_zA_zC(n)=S_zA_z\left(1-\frac{1}{2n^2}-\frac{1}{2n^4}\right),$$

where S_z is the mean stress on the gross cross-sectional area and $n=A_z/(A_z-A_n)$. Equation 6 is derived in [1]. $C(n)$ may be considered to be a correction factor arising from the finite width of the member. It has been shown [3][3] that $C(n)$ is nearly independent of eccentricity in the case of an elliptical hole, and since it is nearly unity in any practical case, eq 6 may be used without serious error for a hole of any shape.

The displacement u_x may be calculated from the stress function given in [2] or by the method of Mushelisvili.

[2] This notation is used throughout for the numbered equations in references.

[3] See p. 545 of reference [3].

II. Displacements

1. Displacement-function method

This method [4] presupposes a knowledge of the Airy stress-function, ϕ. The form of ϕ is exhibited in [2] in terms of curvilinear coördinates (α, β) such that eq 1 of the boundary of the hole reduces to $\alpha=\alpha_0$. The parameters a, b, and c of [2], which, together with α_0, define the shape of the hole, are related to the p, q, and r of eq 1 by

$$e^{\alpha_0}=\frac{p+q}{2},\ abe^{-\alpha_0}=\frac{p-q}{2},\ ac^2e^{-3\alpha_0}=r. \qquad (7)$$

[4] See p. 130 of [3].

The function ψ defined, in the absence of body forces, by

$$\frac{\partial^2\psi}{\partial x\partial y}=\frac{\partial^2\phi}{\partial x^2}+\frac{\partial^2\phi}{\partial y^2}=\nabla^2\phi,$$

with ψ adjusted by means of the arbitrary functions of integration (of the form $f_1(x)+f_2(y)$) so that $\nabla^2\psi=0$, is called the displacement function. The x-component of the displacement is given by

$$u=\frac{1}{E}\frac{\partial\psi}{\partial y}-(1+\nu)\frac{\partial\phi}{\partial x},$$

ere μ is Poisson's ratio. In the present case the y values of u required are u_p, those on the ndary of the perforation. On this (free) ndary, $\partial\phi/\partial x$ is constant, and hence zero, since s even in x and in y. Hence from eq 9,

$$Eu_p=\frac{\partial\psi}{\partial y}\ (\alpha=\alpha_0). \tag{10}$$

According to [2, eq 18],

$$\phi=C_1\phi_1+C_2\phi_2+C_3\phi_3+C_4\phi_4+C_5\phi_5+C_6\phi_6+C_7\phi_7+C_8\phi_8.$$

these terms, all but those in ϕ_1, ϕ_2, and ϕ_3 are rmonic and need not be considered for purposes eq 8. Further, $C_6=0$ for no shear, as shown by eq 23]. Thus only the terms in ϕ_1 and ϕ_2 are uired. From paragraph 5 of [2] ϕ_1 and ϕ_2 are, itting harmonic terms, which disappear for ration ∇^2,

$$\phi_1=4ye^{\alpha}\sin\beta-4abye^{-\alpha}\sin\beta-x^2-y^2,$$

d

$$\phi_2=2ye^{-\alpha}\sin\beta,$$

that

$$\nabla^2\phi_1=8\frac{\partial}{\partial y}(e^{\alpha}\sin\beta-abe^{-\alpha}\sin\beta)-4,$$

d

$$\nabla^2\phi_2=-4\frac{\partial}{\partial y}e^{-\alpha}\sin\beta.$$

Equation 8 becomes

$$\frac{\partial^2\psi}{\partial x\partial y}=C_1\left[8\frac{\partial}{\partial y}(e^{\alpha}\sin\beta-abe^{-\alpha}\sin\beta)-4\right]-4C_2\frac{\partial}{\partial y}e^{-\alpha}\sin\beta,$$

m which

$$\frac{\partial\psi}{\partial x}=C_1\left[8(e^{\alpha}\sin\beta-abe^{-\alpha}\sin\beta)-4y\right]-4C_2e^{-\alpha}\sin\beta+Dx+E, \tag{11}$$

which $Dx+E$ is the most general function of egration of the form $f_1(x)$ which preserves the rmonic character of $\partial\psi/\partial x$. Because ψ is harnic by definition, $\partial\psi/\partial y$ as well as $\partial\psi/\partial x$ is rmonic, and application of the Cauchy-emann test to the expression

$$\frac{\partial\psi}{\partial y}+i\frac{\partial\psi}{\partial x}$$

ows it to be a function of the complex variable $+iy$. Thus $\partial\psi/\partial y$ is the real part of the function of which $\partial\psi/\partial x$ is the imaginary part, so that from eq 11

$$\frac{\partial\psi}{\partial y}=C_1(8e^{\alpha}\cos\beta+8abe^{-\alpha}\cos\beta-4x)+4C_2e^{-\alpha}\cos\beta-Dy+E'.$$

The constants D and E' are obtained by substituting for $\partial\psi/\partial y$ in eq 9, which gives

$$Eu=C_1(8e^{\alpha}\cos\beta+8abe^{-\alpha}\cos\beta-4x)+4C_2e^{-\alpha}\cos\beta-Dy+E'-(1+\nu)\frac{\partial\phi}{\partial x}.$$

For $x=0(\beta=\pm\pi/2)$, $u=0$ for all y, and $\partial\phi/\partial x=0$ by symmetry. Therefore, $D=E'=0$, and

$$\frac{\partial\psi}{\partial y}=C_1(8e^{\alpha}\cos\beta+8abe^{-\alpha}\cos\beta-4x)+4C_2e^{-\alpha}\cos\beta. \tag{12}$$

Substitution of eq 12, with C_1 and C_2 replaced by their values from [2, eq 23] into eq 10 gives

$$\frac{Eu_p}{S_x}=-x_0+\frac{2e^{\alpha_0}\cos\beta}{1-ac^3e^{-4\alpha_0}}(2-ac^3e^{-4\alpha_0}-a^2bc^3e^{-6\alpha_0}),$$

where x_0 is the value of x on the boundary $\alpha=\alpha_0$, which, together with eq 7, gives

$$\frac{Eu_p}{S_x}=-x_0+2\frac{(p+q)^2-2pr}{p+q-2r}\cos\beta. \tag{13}$$

2. Mushelisvili's method

This method, which is treated in detail by Sokolnikoff [4], expresses the stresses, displacements, and the boundary conditions in terms of two analytic functions, ϕ and ψ (not the same as those of the preceding section), of the complex variable $z=x+iy$. The functions ϕ and ψ, which satisfy the problem of [2], have been given by Morkovin [5], who uses the notation

$$s=(p+q)/2,\ t=(p-q)/2,\ r=r, \tag{14}$$

and

$$\zeta=e^{\alpha-\alpha_0}+i\beta, \tag{15}$$

so that the function

$$z=\omega(\zeta)=s\zeta+t/\zeta+r/\zeta^3 \tag{16}$$

maps the boundary $\alpha=\alpha_0$ onto the unit circle $|\zeta|=1$. The value of ζ on the unit circle is denoted by σ; thus $\bar{\sigma}$, the conjugate of σ, is $1/\sigma$. The notation

$$\phi(z)=\phi[\omega(\zeta)]=\phi(\zeta),$$

is used, and similarly for ψ.

The functions ϕ and ψ as found by Morkovin are

$$\phi(\zeta)=sB\zeta+\frac{a_1}{\zeta}-\frac{Br}{\zeta^3},$$

$$\psi(\zeta)=-\left(\frac{s}{\zeta}+t\zeta+r\zeta^3\right)\left(\frac{sB\zeta^4-a_1\zeta^2+3rB}{s\zeta^4-t\zeta^2-3r}\right)-\frac{sB}{\zeta}$$
$$+s(B'+iT_{xy})\zeta-a_1\frac{r}{s}\zeta+Br\zeta^3+Bt\left(1+\frac{r}{s}\right)\zeta,$$

where

$$a_1=Bt\frac{r+s}{r-s}+\frac{B's^2}{r-s}+\frac{iT_{xy}s^2}{r+s},$$

and

$$4B=S_x+S_y,\ 2B'=S_y-S_x.$$

In the present case, $S_y=T_{xy}=0$, giving

$$\phi(\zeta)=\frac{S_x}{4}\left(s\zeta+\frac{a}{\zeta}-\frac{r}{\zeta^3}\right), \tag{17}$$

$$\psi(\zeta)=\frac{S_x}{4}\left[-\left(\frac{s}{\zeta}+t\zeta+r\zeta^3\right)\left(\frac{s\zeta^4-a\zeta^2+3r}{s\zeta^4-t\zeta^2-3r}\right)\right.$$
$$\left.-\frac{s}{\zeta}-2s\zeta-\frac{ar}{s}\zeta+r\zeta^3+t\left(1+\frac{r}{s}\right)\zeta\right], \tag{18}$$

where

$$a=\frac{4a_1}{S_x}=\frac{t(r+s)-2s^2}{r-s}.$$

The rectangular components, u and v, of the displacement are expressed in terms of the functions ϕ and ψ by means of the relation

$$E(u+iv)=(3-\nu)\phi(\zeta)-(1+\nu)\left[\frac{z\overline{\phi}'(\overline{\zeta})}{\overline{\omega}'(\overline{\zeta})}+\overline{\psi}(\overline{\zeta})\right],$$

so that on the boundary $\zeta=\sigma$,

$$E(u_p+iv_p)=(3-\nu)\phi(\sigma)$$
$$-(1+\nu)\left[\frac{\overline{z}\phi'(\overline{\sigma})}{\overline{\omega}'(\overline{\sigma})}+\overline{\psi}(\overline{\sigma})\right].$$

Substitution of the functions ω, ϕ, and ψ from eq 16, 17, and 18 in eq 19 yields, after considerable reduction,

$$\frac{E}{S_x}(u_p+iv_p)=-z_0+2s\sigma+\frac{2s^2-2rt}{s-r}\frac{1}{\sigma},$$

where z_0 is on $\alpha=\alpha_0$, and therefore,

$$\frac{Eu_p}{S_x}=-x_0+\frac{4s^2-2sr-2rt}{s-r}\cos\beta,$$

since $\sigma=e^{i\beta}$ from eq 15.

In terms of the original constants (eq 14), eq becomes,

$$\frac{Eu_p}{S_x}=-x_0+2\frac{(p+q)^2-2pr}{p+q-2r}\cos\beta,$$

which is the same as eq 13.

III. Axial Rigidity

1. General

Substitution of P from eq 6 and u_p from eq 13 into eq 5 gives

$$\frac{1}{K}=1+\frac{t}{A_xlC(n)}\left[-\int x\,dy\right.$$
$$\left.+2\frac{(p+q)^2-2pr}{p+q-2r}\int\cos\beta\,dy\right], \tag{21}$$

where t, the thickness of the plate in which the perforation occurs, is $\int dz$. The two line integrals in eq 21, which are to be taken along half the boundary $\alpha=\alpha_0$, are obtained from eq 1, as

$$\int x\,dy=\frac{1}{2}A_0=\frac{\pi}{2}(pq-3r^2),\ \int\cos\beta\,dy=\frac{\pi q}{2},$$

where A_0 is the area of the perforation.

Equation 21 becomes

$$\frac{1}{K}=1+\frac{V_0}{V_xC(n)}\frac{q(p+q)(p+2q)}{(p+q-2r)(pq-3r^2)}, \tag{22}$$

where $V_0=A_0t$ is the volume of the perforations and $V_x=2A_xl$ is the gross volume of one bay of the member.

For an ellipse, $p=a$, $q=b$, $r=0$, where a and b are the semiaxes (a parallel to the load) and eq 22 reduces to

$$\frac{1}{K}=1+\frac{1+\frac{2b}{a}}{C(n)}\frac{V_0}{V_x},$$

which is the same as [1, eq 48].

It remains to compute the coefficient V_0/V_x in eq 22 for the various cases of interest.

2. Ovaloid; load parallel to long axis

Here $p=2.063$, $q=1.108$, $r=-0.079$ (eq 2). Equation 22 becomes

$$\frac{1}{K}=1+\frac{2.048}{C(n)}\frac{V_0}{V_x}. \tag{23}$$

In practical numerical cases, eq 23 gives substantially the same results as [1, eq 13], derived

a more approximate method. However [1, eq may be used for an ovaloid of which the rec-gular base is not square whereas eq 23 applies y to the shape shown in figure 1.

Ovaloid; load parallel to short axis

In this case, $p=1.108$, $q=2.063$, $r=0.079$. nal 23 becomes

$$\frac{1}{K}=1+\frac{4.968}{C(n)}\frac{V_0}{V_g}. \tag{24}$$

s case and the following cases are not covered previous work.

4. Square with Rounded Corners

For the approximate square of eq 3 and figure 2, $p=q=1$, $r=-0.14$. Eq. 22 becomes

$$\frac{1}{K}=1+\frac{2.989}{C(n)}\frac{V_0}{V_g}, \tag{25}$$

for load parallel to the side of the square.

For load parallel to the diagonal of the square (eq 4) $p=q=1$, $r=0.14$, and eq 22 becomes

$$\frac{1}{K}=1+\frac{3.596}{C(n)}\frac{V_0}{V_g}. \tag{26}$$

IV. Summary

Approximate formulas have been developed for computation of the axial rigidity of a long sion or compression member containing a te of constant thickness uniformly perforated h a series of similar holes of various shapes. axial rigidity factor K is defined so that EA_g is the rigidity that should be used in place EA_g in the ordinary formula for computation the extension of the member.

In many cases of interest the axial rigidity tor K is given by an equation of the form

$$\frac{1}{K}=1+\frac{f}{C(n)}\frac{V_0}{V_g}, \tag{27}$$

ere

$n=A_g/(A_g-A_n)$, A_g being the gross and A_n the net cross-sectional area of the member

$$C(n)=1-\frac{1}{2n^2}-\frac{1}{2n^4}$$

V_0 = the volume of the perforation

V_g = the gross volume of one bay of the member

f = a constant depending on the shape of the perforation and the direction of the applied load.

Values of the constant f for various cases are given in table 1.

TABLE 1.—*Values of f in equation 27*

Perforation	Load parallel to—	f
Ellipse of semiaxes a and b	Major axis, a	1+(2b/a)
Do	Minor axis, b	1+(2a/b)
Ovaloid (fig. 1)	Long axis	2.048
Do	Short axis	4.968
Square (fig. 2)	Side	2.989
Do	Diagonal	3.596

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WASHINGTON, May 21, 1946.

S. Department of Commerce
National Bureau of Standards

Research Paper RP1738
Volume 37, September 1946

Part of the Journal of Research of the National Bureau of Standards

eat Content, Free-energy Function, Entropy, and Heat Capacity of Ethylene, Propylene, and the Four Butenes to 1,500°K[1]

By John E. Kilpatrick[2] and Kenneth S. Pitzer[3]

Values are presented for the following thermodynamic properties for ethylene, propylene and the four butenes, in the ideal gaseous state, to 1,500° K: heat-content function, $(H°-H_0^\circ)/T$; free-energy function, $(F°-H_0^\circ)/T$; entropy, $S°$; heat content, $(H°-H_0^\circ)$; heat capacity, C_p°.

I. Introduction

part of the work of the American ute Research Project 44, this report presents sults of the calculations of the thermody- properties of the heat-content function, nergy function, entropy, heat content, and capacity, in the ideal gaseous state, to ° K, for ethylene, propylene, 1-butene, *cis*- ene, *trans*-2-butene, and isobutene. The cal- ions are based in large part on vibrational encies given in a pending report [4].[4]

n investigation was performed as part of the work of the American m Institute Research Project 44 on the "Collection, Analysis, and tion of Data on the Properties of Hydrocarbons."

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ate Supervisor of the American Petroleum Institute Research ; Professor of Chemistry at the University of California, Berkeley,

s in brackets indicate literature references at the end of this paper.

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II. Unit of Energy and Constants

The unit of energy used in this report is the conventional thermochemical calorie, defined as follows:

1 calorie=4.1833 international joules. (1)

The values of the physical constants used in the calculations are from the "α" tables of the American Petroleum Institute Research Pr 44, which values have been given in an e report from this laboratory [1,23]. The equa for the thermodynamic contributions for t lation and rotation are from the same source and are also reported in reference [1].

The terms for restricted internal rotation computed from the tables of Pitzer and Gwin

III. Method of Calculation

If the complete set of energy levels (quantum states) are known for a given molecule, the values of the thermodynamic functions may be computed exactly. Except for the simpler molecules, the knowledge of the energy levels is not complete enough to permit exact calculation, and certain simplifying assumptions must be introduced regarding the relations among the several kinds of energy levels, as follows: (1) The various vibrations are harmonic; (2) the moment of inertia is not a function of the rotational quantum state; (3) no coupling exists between the vibrational and tional states of energy; (4) if restricted in rotation occurs, the restriction is from a type barrier and no potential coupling between different internal rotations.

The foregoing assumptions, which are marily made in such work and which have made in the present calculations, introduce that are smaller than the uncertainties o presently available experimental data.

IV. Data Used in the Calculation for Ethylene, Propylen *cis*-2-Butene, *trans*-2-Butene, and Isobutene

1. Moments of inertia

(a) Ethylene

Gallaway and Barker [3] have measured the moments of inertia of ethylene accurately from the rotational structure of several infrared bands. Their results have been adopted for the present calculations.

The three moments of inertia are 0.5750×10^{-39}, 2.809×10^{-39}, and 3.384×10^{-39} g cm^2. These moments of inertia are consistent with the following dimensions: Length of C=C bond, 1.353 A; length of C−H bond, 1.071 A; H−C−H angle, 120°. The symmetry number, σ, of ethylene is four. See reference [4].

The entropy of translation and rotation for ethylene gas in the ideal state is then

$$S^\circ_{t+r}=6.524+18.3026\log_{10}T \text{ cal/deg mole.} \quad (2)$$

(b) Propylene

The moments of inertia of propylene and of the butenes were calculated assuming that (1) the C=C and C=H bonds are the same leng in ethylene; (2) the four bonds attached t C=C group are inclined at the same angl in ethylene, namely 120°; (3) the single C−C length is 1.54 angstroms; (4) the ang each methyl group are tetrahedral; (5) the C bond length in a methyl group is 1.09 angst

The three principal moments of iner propylene are 1.9348×10^{-39}, 8.9199×10^{-3} 10.3286×10^{-39} g cm^2. The axis of the sm moment makes an angle of 33°40′ with the C bond. The reduced moment for internal rot is 4.073×10^{-40} g cm^2. The total symm number is three. This number arises w from the symmetry of the internal rotation.

The entropy of translation, over-all rota and free internal rotation for propylene gas i ideal state is

$$S^\circ_{t+r+fr}=11.621+20.5904\log_{10}T \text{ cal/deg mole.}$$

(c) *cis*-2-Butene

The three principal moments of inertia 5.9977×10^{-39}, 14.2431×10^{-39}, and 19.1886×1

g cm². The reduced moments of the two thyl groups have the same value, 5.037×10^{-40} cm². The total symmetry number is 18 which composed of factors of three for each internal tion and two for over-all rotation.

The entropy of translation, over-all rotation and internal rotation for *cis*-2-butene in the ideal eous state is

$$S_{t+r}=11.400+22.8783\log_{10}T \text{ cal/deg mole.} \quad (4)$$

(d) *trans*-2-Butene

The three principal moments of inertia are 675×10^{-39}, 22.440×10^{-39}, and 23.9556×10^{-39}, g cm². The axis of the smallest moment makes angle of 39°58′ with the C=C bond. The reed moment of each of the methyl groups is 98×10^{-40} g cm². The total symmetry number 8, subdivided as in *cis*-2-butene.

The entropy of translation, over-all rotation and internal rotation for *trans*-2-butene in the gas- state is

$$S_{t+r}=10.871+22.8783\log_{10}T \text{cal/deg mole.} \quad (5)$$

(e) Isobutene (2-methylpropene)

The three principal moments of inertia are 842×10^{-39}, 10.7646×10^{-39}, and 18.6968×10^{-39}, g cm². The reduced moment of each of the two thyl groups is 4.999×10^{-40} g cm². The total mmetry number is 18, subdivided as in *cis*-2- tene.

The entropy of translation, over-all rotation, d free internal rotation, for isobutene gas in the al gaseous state is:

$$S_{t+r}=11.482+22.8783\log_{10}T \text{ cal/deg mole.} \quad (6)$$

2. Vibrational frequencies

(a) Ethylene

The vibrational assignment of Gallaway and rker [3] has been adopted. The 12 vibrations are divided into 7 symmetry types. The frequencies of these vibrations, in wave numbers and classified according to symmetry, are listed in the following tabulation:

Symmetry: point group V_h

A_{1g}	3019. 3	B_{2u}	3105. 5
	1623. 3		995. 0
	1342. 4	A_{1u}	825
B_{2g}	2989. 4	B_{2g}	943
	1443. 9	B_{1u}	949. 2
B_{1g}	3069		
	1055		

(b) Propylene

The only symmetry element of the propylene molecule is the plane of the skeletal frame, C=C−C. The 20 vibrations can therefore be divided into only two classes.

The argument for the following assignment is given in a preceding report [4]. The description of the motion involved is only approximate. The frequencies are given in wave numbers, cm^{-1}:

Symmetry: point group C_s

A′	A″	
3050(3)	----	C−H stretching (ethylenic)
2950(2)	2950	C−H stretching (methyl)
1649	----	C=C stretching
1444	1444	CH_3 $\delta(\pi)$
1415	----	CH_2 δ
1370	----	CH_3 δ (σ)
1297	990	CH wagging
------	580	C=C twisting
1042	1050	CH_3 wagging
1172	911	CH_2 wagging
930	----	C−C stretching
417	----	Skeletal bending

(c) *cis*-2-Butene

The symmetry of *cis*-2-butene allows its 28 vibrations to be classified into four symmetry types. A discussion of the following assignment may be found in another report [4]. The frequencies are given in wave numbers, cm^{-1}:

Symmetry: point group C_{2v}

A_1	A_2	B_1	B_2	
3050	----	----	3050	C−H stretching (ethylenic)
2950(2)	2950	2950	2950(2)	C−H stretching (methyl)
1672	----	----	----	C=C stretching
876	----	----	986	C−C stretching
1450	1450	1450	1450	CH_3 δ (τ)
1380	----	----	1380	CH_3 δ (σ)
1267	----	----	1390	C−H wagging, planar
----	1050	673	----	C−H wagging, non planar
1018	----	----	1064	CH_3 wagging, planar
----	950	1040	----	CH_3 wagging, nonplanar
304	----	----	581	Skeletal bending
----	402	----	----	C=C twisting

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(d) *trans*-2-Butene

Although this isomer has the symmetry C_{2h} instead of the C_{2v} of *cis*-2-butene, the two point groups are isomorphic and the classifications the frequencies are quite similar [4]:

Symmetry: point group C_{2h}

A_g	A_u	B_g	B_u	
3050	----	----	3050	C—H stretching (ethylenic)
2950(2)	2950	2950	2950(2)	C—H stretching (methyl)
1681	----	----	----	C=C stretching
870	----	----	1065	C—C stretching
1450	1450	1450	1450	CH_3 δ (π)
1389	----	----	1375	CH_3 δ (σ)
1309	----	----	1304	C—H wagging, planar
----	964	746	----	C—H wagging, nonplanar
1080	----	----	973	CH_3 wagging, planar
----	1030	1043	----	CH_3 wagging, nonplanar
507	----	----	290	skeletal bending
----	240	----	----	C=C twisting

(e) Isobutene

Isobutene has the same symmetry as *cis*-2-butene, C_{2v}, but the presence of both methyl groups on the same end of the C=C frame ma a slightly different description of the vibrati necessary [4]:

Symmetry: point group C_{2v}

A_1	A_2	B_1	B_2	
3050	----	----	3050	C—H stretching (ethylenic)
2950 (2)	2950	2950	2950 (2)	C—H stretching (methyl)
1664	----	----	----	C=C stretching
800	----	----	986	C—C stretching
1450	1450	1450	1450	CH_3 δ (π)
1380	----	----	1380	CH_3 δ (σ)
1390	----	----	------	CH_3
----	----	----	1280	CH_2 wagging, planar
----	----	888	------	CH_2 wagging, nonplanar
1053	----	----	1007	CH_3 wagging, planar
----	988	1066	----	CH_3 wagging, nonplanar
378	----	391	431	Skeletal bending
----	700	----	----	C=C twisting

3. Potential barriers restricting internal rotation

(a) Propylene

A threefold cosine type barrier of 1,950 cal/mole, when combined with the previously mentioned constants, was found to give results agreeing satisfactorily with the experimental values of the entropy [5] and the gaseous heat capacity [6].

(b) *cis*-2-Butene

A threefold restricting potential of 450 cal/mole for each methyl group was found to give satisfactory agreement with the experimental values of the entropy [7] and the gaseous heat capacity [8].

This abnormally low value probably arises from the opposing effects of the normal methyl barriers and steric hindrance between the two methyl groups.

The assumption of independent cosine ty barriers is probably poorer in *cis*-2-butene than the other members of this family. The symm try of the internal rotations prohibits exactly t type of barrier. However, the effective height the barrier for any reasonable shape is so l that the details of the shape have relatively lit effect upon the thermodynamic functions.

(c) *trans*-2-Butene

The potential barrier giving the best agreeme with the experimental values of the entropy and the gaseous heat capacity [8] was found to 1,950 cal/mole.

This value agrees, as it should, with that propylene. There is probably little or no pote tial coupling between the two methyl groups increase the apparent height of the barrier.

Additional confirmation for this value is giv

the 210 cm^{-1} Raman line of *trans*-2-butene. several methods a barrier height of about 2,000 mole can be calculated if this line is assigned $_8$ internal rotation.

(d) Isobutene

n this case a value of 2,350 cal/mole gives the agreement with the experimental values of entropy [10] and the gaseous heat capacity [11].

This apparent increase from the value 1,950 cal/mole found for propylene and *trans*-2-butene is undoubtedly due to the neglected potential coupling terms between the two methyl rotations. The phenomenon is similar to the apparent barrier increase in the series ethane, propane, isobutane and neopentane. Preliminary calculations upon the thermodynamic effect of such coupling indicate that this explanation is valid.

V. Data Used in the Calculations for 1-butene

1. Vibrational frequencies and moments of inertia

n the basis of the information and data avail- at the present time, it does not seem feasible make a satisfactory vibrational assignment in il for 1-butene. The symmetry of the mole- is so low that a normal coordinate analysis of ibrations would be very difficult. The situ- n is further complicated by the unsymmetrical tion in the skeleton of the molecule. In the t of these difficulties it was decided to use a empirical approach to the calculation of the modynamic functions for 1-butene.

he thermodynamic effect of the vibrations was n to be the same as that of the 20 frequencies propylene, the 6 characteristic frequencies of methylene group [12], 1 C—C stretching fre- cy of 995 cm^{-1}, and 1 skeletal bending fre- cy of 320 cm^{-1}. This last frequency was en from the Raman spectrum [13], and its gnment, although somewhat doubtful, appears ified because 1-butene should possess a etal bending mode of vibration of about this nitude, on the basis of analogous molecular ctures.

he moments of inertia were calculated from dimensions used for propylene, with the axis he methyl group lying 60° out of the plane of extended or *trans* configuration of the carbon eton. The reason for this choice is discussed r. The product of the three principal moments nertia is calculated to be $2{,}232\times10^{-117}$ g^3 cm^6. he potential barrier restricting the rotation of methyl group was taken to be 3,400 cal/mole, n propane.

2. Internal (Skeletal) Rotation

he only remaining factor to be considered is skeletal rotation. The use of Fisher-Hirschfelder molecular models proved quite helpful in this regard. If it were not for the steric interference of the methyl and the ethylenic groups, there would probably be three equivalent minima at 60°, 180°, and 300°, counting from the extended, planar configuration The two groups apparently interfere enough to raise the minimum at 180° by several thousand calories. The unperturbed barrier would be expected to be about the same height as in propylene or *trans*-2-butene. This steric interference would then have the effect of making the rotational potential energy almost constant from 120° to 240° in the angle of rotation. There undoubtedly is not complete cancellation of this minimum. The large number of Raman lines indicates more than one kind of skeletal minimum. However, for thermodynamic purposes, the details of the barrier in this region are relatively unimportant.

The following potential satisfies the above requirements:

$$V=(1/2)V_0(1-\sin 3\phi),\quad -120°\leq\phi\leq120°$$
$$V=V_0,\qquad\qquad 120°\leq\phi\leq240° \quad (7)$$

The classical form of the partition function is a satisfactory approximation to the exact partition function when, as is true in this molecule, the reduced moment of inertia for the rotation is several times the moment of inertia of a methyl group.

When these calculations were made, an exact formula for the proper reduced moment of inertia for the skeletal rotation was not available, and an estimated value of 20×10^{-40} g cm^2 was used. Since then, the theory has been developed further [21], but the minor changes required seemed unjustified in view of the approximate character of other parts of the calculations for 1-butene. This matter is discussed further below.

The rotational partition function is given by the expression

$$Q=Q_f\left(\frac{1}{2\pi}\right)\int_0^{2\pi}e^{-V/RT}d\phi, \tag{8}$$

where Q_f is the usual partition function for free rotation, V the potential barrier as a function of ϕ, R the gas constant, and T the absolute temperature.

When eq 7 and 8 are combined, the following relations may be derived:

$$Q/Q_f=e^{-x}\left(\frac{2}{3}I_0(x)+\frac{1}{3}e^{-x}\right) \tag{9}$$

$$(F_f-F)/RT=-x+\ln\left(\frac{2}{3}I_0(x)+\frac{1}{3}e^{-x}\right) \tag{10}$$

$$H_r/RT=(1/2)+x-\frac{x(2I_1(x)-e^{-x})}{2I_0(x)+e^{-x}} \tag{11}$$

$$C_r/R=(1/2)+x^2-\frac{2xI_1(x)}{2I_0(x)+e^{-x}}$$

$$-x^2\left(\frac{2I_1(x)-e^{-x}}{2I_0(x)+e^{-x}}\right)^2. \tag{12}$$

In eq 9 to 12, $x=V_0/2RT$, $I_n(x)=i^{-n}J_n(ix)$. $J_n(y)$ is the ordinary Bessel function of the first kind. $I_n(x)$ is real when x is real. $(F_f-F)/T$, H_r/T, and C_r are the differences in the free-energy function for free and restricted rotation, the heat-content function and the heat capacity for restricted rotation, respectively. In the last two cases (eq 11 and 12), the term 1/2 is the limit of H_r/RT and C_r/R as x (and V_0) approach zero. It is therefore the usual heat-content function and heat-capacity contribution for free rotation.

It was found that the best agreement with the experimental equilibrium data on the isomerization of the *n*-butenes [14, 15, 16] could be obtained with V_0=2,400 cal/mole. This comparison is presented in reference [17]. This value is reasonable in magnitude on physical grounds and in addition gives good agreement with the abovementioned experimental equilibrium data over a wide temperature range.

The value for the entropy of 1-butene in ideal gaseous state at 266.91° K obtained application of the third law to appropriate calmetric data is 70.87 ±0.20 cal/deg mole The present calculations yield 71.19 cal/deg for the same temperature. A slightly hig barrier to internal rotation would lower the culated value of the entropy, but would make good the agreement with the equilibrium data. view of the possibility of some end-for-end randness of position of 1-butene molecules in the tal, which would leave some residual entropy included in the experimental value, it seemed to retain the good accord with the equilibriu

After the present calculations were comple the paper by Aston, Szasz, Woolley, and Brwedde [22] was published which includes calctions for 1-butene and reports values for specific heat of the gas. The present aut cannot agree with the assertion of Aston et al. that "the Raman and infrared spectra indi essentially only one form," because their asment leaves three Raman lines having frequen below 600 cm^{-1} unexplained.

The values of specific heat for gaseous 1-bu are reported in reference [22] as unpublished of Scott and Wacker with no details being gi Hence, although the present calculations y values of heat capacity which are higher than values of Scott and Wacker by about 0.7 cal mole, it does not seem justified to make extens revisions until additional experimental data come available.

The use of the exact moment of inertia skeletal internal rotation calculated by the recedeveloped methods [21], 18.2×10^{-40} g cm^2, whave the effect of leading to a potential barr2,240 cal/mole for the skeletal motion and a capacity about 0.05 cal/deg mole lower in range of 300° to 400°K. Other changes o easily be justified in the vibrational assignmen obtain agreement with the experimental gas specific heat values. However, these chan would make slightly greater the difference betw observed and calculated values of the entropy

VI. Results

Tables 1 to 5 present values for the free-energy function, the heat-content function, the entropy, the heat content, and the heat capacity, to 1,500° K, for the six compounds considered in this report.

Table 6 contains a comparison of the calculated values with the available calorimetric data on heat capacity and entropy. The agreement is seen to be best for ethylene, in which case the spectroscopic data are of considerably higher reliability than for the higher olefins. Ethylene has, in addition, the complication of internal rotation. For propylene and *trans*-2-butene the agreement is good. There is a somewhat larger discrepancy in the case of isobutene. The calculated values of the heat capacity in these three cases increase a little too rapidly with temperature.

The unusually complicated nature of the restricting potential in *cis*-2-butene probably accounts for the relatively less satisfactory agreement in that case. It is planned to perform in the future a more detailed study of the problem regarding the *cis*-2-butene molecule.

TABLE 1.—*Values[a] of the heat-content function, $(H°-H_0^\circ)/T$, for the six monoolefins, C_2 to C_4, for the ideal gaseous state, to 1,500° K*

Compound (gas)	Formula	Temperature[a] in °K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
		Heat Content Function,[b] $(H°-H_0^\circ)/T$, in cal/deg mole														
ne (ethylene)	C_2H_4	0	8.47	8.48	9.28	10.23	11.22	12.18	13.10	13.96	14.76	15.52	16.22	16.88	17.50	18.07
ne (propylene)	C_3H_6	0	10.86	10.88	12.48	14.15	15.82	17.42	18.94	20.36	21.69	22.92	24.07	25.13	26.12	27.05
ene	C_4H_8	0	14.17	14.21	16.72	19.26	21.69	23.96	26.07	28.02	29.83	31.51	33.06	34.49	35.82	37.06
Butene	C_4H_8	0	13.23	13.27	15.36	17.68	20.01	22.26	24.39	26.38	28.23	29.96	31.57	33.06	34.45	35.74
-Butene	C_4H_8	0	14.05	14.10	16.46	18.84	21.16	23.37	25.43	27.38	29.19	30.87	32.43	33.88	35.22	36.47
thylpropene (isobutene)	C_4H_8	0	13.69	13.74	16.30	18.83	21.25	23.50	25.62	27.56	29.37	31.06	32.63	34.08	35.42	36.67

Interpolation to other temperatures in the interval 298.16° to 1,500°K may be made by appropriate graphical or analytical methods. For temperatures between 20° and 298.16°K, values may be estimated by extrapolating the values for 300°, 400°, 500° and 600°K. The values in this table are given to more significant figures than are warranted by the absolute accuracy of the individual values in order to retain the internal consistency of the several thermodynamic functions of a single substance, and also to retain the significance of the increments with temperature of a given thermodynamic function.

[b] The heat-content function, $(H°-H_0^\circ)/T$, is the heat content at the given temperature less the heat content at 0°K, divided by the absolute temperature for the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atmosphere).

TABLE 2.—*Values[a] of the free-energy function, $(F°-H_0^\circ)/T$, for the six monoolefins, C_2 to C_4, for the ideal gaseous state to 1,500° K*

Compound (gas)	Formula	Temperature[a] in °K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
		Free-energy function,[b] $(F°-H_0^\circ)/T$, in cal/deg mole														
ne (ethylene)	C_2H_4	0	−43.98	−44.03	−46.61	−48.74	−50.70	−52.50	−54.19	−55.78	−57.29	−58.74	−60.12	−61.44	−62.71	−63.94
ne (propylene)	C_3H_6	0	−52.95	−53.02	−56.39	−59.32	−62.05	−64.61	−67.04	−69.36	−71.57	−73.69	−75.73	−77.70	−79.60	−81.43
ene	C_4H_8	0	−59.32	−59.41	−63.87	−67.84	−71.56	−75.08	−78.42	−81.61	−84.66	−87.58	−90.39	−93.09	−95.70	−98.21
Butene	C_4H_8	0	−58.67	−58.75	−62.89	−66.51	−69.94	−73.19	−76.30	−79.29	−82.17	−84.95	−87.62	−90.20	−92.70	−95.12
-Butene	C_4H_8	0	−56.80	−56.89	−61.31	−65.19	−68.84	−72.27	−75.53	−78.64	−81.62	−84.47	−87.22	−89.87	−92.44	−94.91
thylpropene (isobutene)	C_4H_8	0	−56.47	−56.56	−60.90	−64.77	−68.42	−71.88	−75.15	−78.29	−81.29	−84.17	−86.94	−89.60	−92.17	−94.66

[a] See footnote "a" of table 1.

[b] The free-energy function, $(F°-H_0^\circ)/T$, is the free energy at the given temperature less the heat content at 0° K, divided by the absolute temperature for the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atmosphere).

TABLE 3.—*Values* [a] *of the entropy, $S°$, for the six monoolefins, C_2 to C_6, for the ideal gaseous state, to 1,500° K*

Compound (gas)	Formula	Temperature [a] in °K													
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400
		Entropy [b], $S°$, in cal/deg mole													
Ethene (ethylene)	C_2H_4	0	52.45	52.51	55.89	58.98	61.92	64.68	67.28	69.74	72.06	74.26	76.34	78.32	80.21
Propene (propylene)	C_3H_6	0	63.80	63.90	68.86	73.47	77.87	82.04	85.98	89.72	93.26	96.61	99.80	102.84	105.98
1-Butene	C_4H_8	0	73.48	73.62	80.59	87.09	93.25	99.05	104.50	109.63	114.49	119.09	123.45	127.59	131.52
cis-2-Butene	C_4H_8	0	71.90	72.02	78.25	84.19	89.95	95.46	100.69	105.67	110.40	114.91	119.19	123.26	127.15
trans-2-Butene	C_4H_8	0	70.86	70.98	77.76	84.04	90.00	95.64	100.97	106.02	110.81	115.34	119.65	123.75	127.66
2-Methylpropene (isobutene)	C_4H_8	0	70.17	70.30	77.21	83.60	89.67	95.38	100.77	105.85	110.66	115.23	119.58	123.68	127.59

[a] See footnote "a" of table 1.

[b] $S°$ is the entropy (exclusive of nuclear spin) of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atmosphere) at temperature indicated.

TABLE 4.—*Values* [a] *of the heat content, $(H°-H_0^\circ)$, for the six monoolefins, C_2 to C_6, for the ideal gaseous state, to 1,500°*

Compound (gas)	Formula	Temperature [a] in °K													
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400
		Heat content, [b] $(H°-H_0^\circ)$, in cal/mole													
Ethene (ethylene)	C_2H_4	0	2525	2544	3711	5117	6732	8527	10480	12560	14760	17070	19470	21950	24490
Propene (propylene)	C_3H_6	0	3237	3265	4990	7076	9492	12200	15150	18320	21690	25210	28880	32670	36570
1-Butene	C_4H_8	0	4224	4263	6687	9629	13010	16770	20860	25220	29830	34660	39670	44840	50150
cis-2-Butene	C_4H_8	0	3981	3981	6144	8839	12010	15580	19510	23740	28230	32960	37880	42960	48250
trans-2-Butene	C_4H_8	0	4190	4228	6582	9422	12660	16300	20350	24640	29190	33960	38920	44080	49310
2-Methylpropene (isobutene)	C_4H_8	0	4082	4121	6522	9414	12750	16450	20490	24800	29370	34170	39150	44300	49590

[a] See footnote "a" of table 1.

[b] $(H°-H_0^\circ)$ is the heat content at the given temperature less the heat content at 0° K of the given hydrocarbon in the thermodynamic standard gas state of unit fugacity (1 atmosphere).

TABLE 5.—*Values* [a] *of the heat capacity, C_p°, for the six monoolefins, C_2 to C_6, for the ideal gaseous state, to 1,500°K*

Compound (gas)	Formula	Temperature [a] in °K													
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400
		Heat capacity, [b] C_p°, in cal/deg mole													
Ethene (ethylene)	C_2H_4	0	10.41	10.45	12.90	15.16	17.10	18.76	20.20	21.46	22.57	23.54	24.39	25.14	25.79
Propene (propylene)	C_3H_6	0	15.27	15.34	19.10	22.62	25.70	28.37	30.68	32.70	34.46	35.99	37.32	38.49	39.51
1-Butene	C_4H_8	0	21.35	21.45	26.94	31.75	35.82	39.31	42.33	44.95	47.24	49.23	50.96	52.47	53.79
cis-2-Butene	C_4H_8	0	18.86	18.96	24.33	29.39	33.80	37.60	40.87	43.70	46.15	48.28	50.13	51.74	53.13
trans-2-Butene	C_4H_8	0	20.99	21.08	26.02	30.68	34.80	38.38	41.50	44.20	46.58	48.65	50.44	52.00	53.36
2-Methylpropene (isobutene)	C_4H_8	0	21.30	21.39	26.57	31.24	35.30	38.81	41.86	44.53	46.85	48.88	50.63	52.17	53.51

[a] See footnote "a" of table 1.

[b] C_p° is the heat capacity at constant pressure of the given hydrocarbon in the thermodynamic standard gaseous state of unit fugacity (1 atmosphere) at temperature indicated.

TABLE 6.—*Comparison of experimental and calculated values of entropy and gaseous heat capacity*

Temperature (°K)	Heat capacity, C_p° (cal/deg mole)		Entropy, S° (cal/deg mole)	
	Calculated	Experimental	Calculated	Experimental
ETHYLENE				
[illegible]			47.35	47.36 [19]
[illegible]	9.77	9.74 [20]		
[illegible]	10.45	10.39 [20]		
[illegible]	10.96	10.99 [20]		
PROPYLENE				
[illegible]			59.90	59.90 [5]
[illegible]	15.27	15.42 [6]		
[illegible]	16.63	16.74 [6]		
[illegible]	17.88	17.93 [6]		
***cis*-2-BUTENE**				
[illegible]			68.46	68.58 [7]
[illegible]			70.74	70.87 [7]
[illegible]	18.86	19.14 [7, 8]	71.90	72.02 [7]

TABLE 6.—*Comparison of experimental and calculated values of entropy and gaseous heat capacity*—Continued

Temperature (°K)	Heat capacity, C_p° (cal/deg mole)		Entropy, S° (cal/deg mole)	
	Calculated	Experimental	Calculated	Experimental
***cis*-2-BUTENE**—continued				
332.85	20.74	20.96 [7, 8]		
371.24	22.80	22.95 [7, 8]		
***trans*-2-BUTENE**				
274.04			69.13	69.12 [9]
298.16	20.99	20.96 [8]		
332.90	22.72	22.69 [8]		
371.50	24.63	24.53 [8]		
ISOBUTENE				
240.00	18.24	18.17 [11]	65.87	65.86 [10]
272.16	19.87	19.81 [11]		
312.16	22.04	21.91 [11]		
353.16	24.20	23.96 [11]		

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WASHINGTON, May 9, 1946.

S. Department of Commerce
tional Bureau of Standards

Research Paper RP1739
Volume 37, September 1946

Part of the Journal of Research of the National Bureau of Standards

A Simple Cyclic Falling-Film Molecular Still

By John Keenan Taylor

The efficient cyclic falling-film molecular still described is characterized by simplicity of operation and ease of construction. The liquid to be distilled is pumped from the reservoir and introduced on the vertical cylindrical evaporator by an annular orifice. The resulting uniform distribution of the distilland, together with the short column used, makes for efficient operation. The apparatus may be used for charges of liquid ranging from a minimum of about 10 ml to 1 liter or more.

I. Introduction

Molecular distillation is becoming of increasing terest for the separation and purification of y kinds of materials. For example, the proc- akes possible the separation of constituents tural oils, fats, and waxes which have for- y been considered undistillable. [5, 6]* A ber of stills have been described in the ature for utilizing this method, ranging in from those intended for handling a few drops material to those capable of dealing with tank- quantities. When small volumes of material involved, of the order of a few milliliters or , the experimenter is limited to the compara- ly inefficient pot still. When larger amounts at hand, cyclic falling-film stills are much to preferred.

It has been emphasized [2, 4, 6, 8] that mole- r distillation, or free evaporation as it is also d, takes place only from an extremely thin face layer of the distilland. Hence, it is of most importance that this layer at all times be resentative of the bulk of the liquid. The face is being continually impoverished by pref- ntial escape of the more volatile components, that some means of maintaining the equilibrium ween bulk and surface concentration must be vided. In pot stills convection and diffusion are depended upon to renew the surface, and the ineffectiveness of these processes at high rates of distillation is reflected in the inefficiency of the apparatus. For this reason, stills in which a thin film of distilland is flowed over a heated surface, so that the distilling layer is chiefly the entire bulk of the liquid, have supplanted the older pot type wherever practicable. The film still has the added advantage of minimizing the time that the liquid is held at an elevated temperature, which is a very important consideration when dealing with thermally unstable materials.

The chief problem involved in the design of falling-film stills is to provide for uniform distribution of the distilland on the surface of the evaporator. Failure to do so results in preferential distillation of the more readily heated thinner layers, and consequently a tendency to approach bulk distillation rather than surface evaporation. A number of devices have been suggested to overcome this difficulty. These have consisted of embossed designs on the surface of the evapora-

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*Figures in brackets indicate literature references at the end of this paper.

tor [6], cascade dividers [1], rotating distributors [7], coating the column with ground glass [3], and like measures. One group of investigators made use of a serrated distributor at the top of the column and a wire wound spirally around the column to facilitate the distribution of the liquid [9]. Detwiler and Markley [3] claim good results by admitting the distilland at the top of the column by means of a tapered sleeve guide, by providing a mushroom head at the top of the column, and coating the entire evaporator with fragmented glass. On the mechanical side, Quackenbush and Steenbock [10] have described a still in which a magnetically operated rotor continually wipes the evaporating film. The highly efficient but complicated rotary-film stills of Hickman [6] may be considered as the ultimate in design for minimizing the difficulties inherent in the distribution of the distilland.

Most of the devices suggested to increase the efficiency of molecular stills appear to be either of doubtful value or else require cumbersome and expensive mechanical equipment for their utilization. The still described in this paper achieves excellent distribution of the evaporating film by a simple and easily constructed device. In addition, it incorporates some of the best features of those already described.

II. Description of Apparatus

The features of design that have been aimed for in this still are [a] excellent distribution of distilling layer of liquid, [b] a short column to minimize impoverishment of the distilling surface, and [c] high ratio of rate of renewal of surface to rate of distillation. The apparatus is shown diagramatically in figure 1. The still proper is indicated by *M*. It consists of a central evaporator, *E*, surrounded by a condensing surface. The distinctive feature of the apparatus is the system for distributing the liquid upon the surface of the evaporator. A tube of internal diameter slightly larger than the outside diameter of the evaporator is placed over the top portion of it so that an annular orifice of uniform dimensions is formed. The operation is as follows. As the liquid is pumped into this distributor, a head is built up until the integrated rate of flow from the orifice equals the delivery rate of the pump. In practice a head of about 1 to 2 cm is maintained so that a continuous supply of liquid to the evaporator is assured. When carefully constructed, this annulus produces a film which starts uniformly around the entire surface of the evaporator and which persists as it falls.

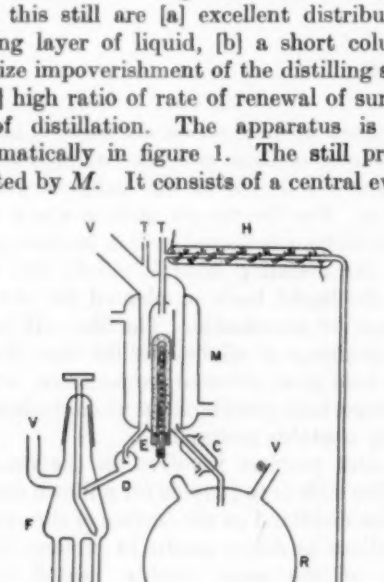

FIGURE 1.—*Molecular still*

A, Ampoules; *C*, cooler; *D*, drop counter; *E*, evaporator; *F*, fraction collector; *H*, preheater; *P*, pump; *R*, reservoir; *S*, solenoid; *T*, thermocouple outlets; *V*, vacuum leads.

Since the apparatus should prove useful for a number of applications, the details of its construction will be given. Evaporator, *E*, is made from a glass tube 18 mm in diameter [1] the outside surface of which had been finely ground to facilitate the distribution of the liquid. A heater of nichrome wire contained in a 7-mm tube is placed in the center, and the space between it and the wall of the evaporator is filled with 2-mm lengths of bare copper wire to facilitate heat distribution. The "bonnet" for distributing the liquid on the column is of 22-mm tubing (19-mm i. d.) so that an annulus of about 0.5-mm width is formed. A metal shim, which was subsequently dissolved

[1] The apparatus is constructed of ordinary Pyrex glass tubing of standard wall thickness. All sizes are the nominal outside dimension unless otherwise stated.

served to space this tube during the fabrication. The bonnet extends for a distance of about mm over the evaporator, there being exposed a mm length of evaporating surface. The shortof the evaporator follows the recommendation awcett [4], who showed that long columns have creased efficiency.

he concentric condenser, surrounded by a r jacket, is of 45-mm tubing. The minimum or path between the evaporator and condenser us about 12 mm. A vacuum lead of 20-mm ng is ample to remove residual gas and mposition products formed during the distion.

he bottom of the still is arranged with two entric gutters that carry distillate to fraction ctor, F, and residue to reservoir, R, respecly.

hermocouples are inserted at T to measure the perature of the incoming liquid and also to sure the temperature of the falling film, if so red. A thermocouple inserted at the copper- interface in E measures the temperature of vaporator.

ooler, C, may be used to cool the liquid as it s the still and enters the reservoir, if this is ble. The reservoir, R, is made from a -bottom flask of one liter capacity.[2] It is ded with a vacuum lead, V, and a tube for introduction of the material to be distilled. ale standard-taper ground joint sealed to R, the top, and normally closed with its female lement offers a convenient means for introng samples without danger of contamination stop-cock grease. (This arrangement is not n in the figure.) An electric heater may also laced around the bottom of R to assist in the liminary degassing of the liquid.

he pump circulates liquid from R to the still. nsists of a solenoid-operated hollow piston, P, el with a bronze-ball lift valve seating on its al surface. The diameter of the piston is en so that a reasonably close fit with the body e pump is obtained. A tight fit is neither ssary nor desirable. Only a slight loss of ping efficiency results from a loose fit, while a means to drain the apparatus is gained. Lifting the steel-ball check valve with a magnet also aids the drainage operation. A steel ball on a ground-glass seat acts as a check valve. These metal parts are gold-plated to minimize corrosion. Nichrome wire springs inserted above and below the piston serve to protect the glass walls of the pump in the event of faulty operation. The glass body of the pump is made from 10-mm tubing, and its overall length is about 10 cm. The tubes leading to and from the pump are 4-mm in diameter. By keeping these parts small, the minimum operating volume is about 10 ml.[3]

The solenoid, S, contains 4,000 turns of No. 24 enameled, cotton-covered wire on a suitable brass spool enclosed in a case with steel ends and outer shell. The solenoid operates, in series with a suitable resistance, on the 115-v d-c line and is actuated by a relay controlled by an electronic impulse timer previously described [11]. By regulating the length of stroke, governed by the current in the solenoid, and the rate of pulsing, the pumping rate can be readily adjusted and controlled.

The sample collector, F, is similar to one described by Waddle [12]. It is constructed from a 125-ml Erlenmeyer flask to which is sealed a 19/38 standard-taper joint, as shown in the figure. This joint may be rotated to permit distillate to collect in any one of the four or five ampoules sealed to the bottom of the flask. A vacuum lead, V, is provided to assist in the evacuation of the apparatus.

The entire apparatus is mounted on a frame 15 inches wide and 30 inches high. The leads, V, are joined to a common tube which is in turn sealed to a conventional portable vacuum system consisting of fore vacuum pump, diffusion pump, traps, and MacLeod gage, all mounted on a frame of dimensions similar to those of the still. By cutting the one connecting lead, the two units may be easily transported to various locations in the laboratory.

dvantage is gained by using a smaller vessel when dealing with quantities. In either case the entrance tube leading in from the still be placed so that it is directed toward the exit sump of the reservoir ase the drainage hold-up for small volumes of liquid.

[3] Pumps operating in high vacuum are either lift or force pumps, and hydrostatic head of liquid above the check valve is the factor that replenishes the chamber of the pump. The minimum operating volume of the pump includes the volume contained in the lead tube up to the level of the check valve, the volume of the pump chamber, and the volume of liquid contained in the tube leading from the pump to the still proper. This, together with the drainage of the still and reservoir, constitutes the hold-up of the apparatus. The dimensions of the pump and tubes must be kept small to minimize this hold-up. Lift pumps, such as the one used here, appear to offer the greatest possibilities for combining the opposing characteristics of low hold-up and large pumping capacity.

III. Method of Operation

The method of operation is essentially as follows. The liquid to be distilled is placed in *R* and the introduction tube sealed or closed off with a ground joint. The system is then evacuated during which, at first, large quantities of dissolved gas are liberated. Reservoir, *R*, may be warmed with the heater provided for this purpose, to help remove gas. When evolution of gas ceases or slows down, the pump is operated, and the liquid is allowed to flow over the cold surface of the evaporator. Usually only a few cycles of flow are required to produce a perfectly quiet distillation. Warming the evaporator to a temperature that is insufficient to cause appreciable distillation greatly facilitates the degassing process.

The distillation is started when the pressure of the system reaches 10^{-4} mm of mercury or lo The heater imbedded in the evaporator and t one located at *H* are connected to adjustable vo age transformers and regulated so that the temp ature of the incoming liquid is about equal to th of the evaporator. The pumping rate is adjust so that approximately 1 ml/sec is circulated arou the system. A high ratio of rate of flow to rate distillation is desirable, as under this condition operation, the chance for formation of stagna layers of distilland on the surface of the evapora is decreased. The distillate is collected in suita fractions in the ampoules, *A*, sealed to *E*. At t end of the distillation, the residue containing t less volatile components is removed at the bre off tip drain shown near the bottom of the pum

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WASHINGTON, May 17, 1946.

S. Department of Commerce
tional Bureau of Standards

Research Paper RP1740
Volume 37, September 1946

Part of the Journal of Research of the National Bureau of Standards

Study of Resinous Sealants for Porous Metal Castings

By Vernon C. F. Holm

The repair of porous castings by sealing with liquid synthetic resins was investigated. The sealing efficiencies of fourteen resins were determined on porous bushings of aluminum, a copper-silicon alloy, and a red brass, impregnated by the vacuum-pressure method. Tests were made to determine the durability of the two most promising sealants by exposing specimens sealed with these resins to hot motor oil, high octane gasoline, boiling water elevated temperatures, high pressures, and thermal shock. The results suggest that this procedure for rendering porous castings pressure tight may be permissible in emergencies but that, in general, the foundryman should exert every effort to produce non-porous castings instead of trying to remedy porosity.

I. Introduction

The production of castings capable of retaining uids or gases under pressure is a foundry prob- that frequently entails considerable diffi- lties. Porous castings may result from (1) the e of a metal that has an inherent tendency wards microporosity, (2) incorrect foundry hniques, or (3) design requirements that do not ovide for adequate feeding during solidification, . In any case internal cavities exposed during chining may provide passageways for leakage en the castings are placed in service.

Some alloys which have rather wide solidifica- n ranges, such as certain magnesium alloys, are ite susceptible to microshrinkage. Castings of agnesium alloys, used as containers for fluids der slight pressure, therefore are frequently ated with sealants to prevent leakage. Such atments have been satisfactory in light-metal tings for low pressure service, but the problem eliminating porosity in castings of other metals t have to operate under more severe conditions temperature and pressure, is more difficult.

During the recent war period when a high rate of production of vital war materials was essential, the output of pressure-tight bronze castings of certain hydraulic marine fittings and other castings was seriously hampered because of porosity rejections. In instances where the mechanical strength of the fittings was ample, in spite of the porosity, it was suggested that leaky castings could be salvaged through the use of suitable sealants as in the case of the lighter alloys. Although con-

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siderable work was done in this connection, very little information has been published on the subject. Some of the materials that have been tried are linseed oil [1, 2] [1], shellac [2], sodium silicate solutions [2, 3], and various types of synthetic resins [2, 3, 4, 5]. In the case of castings of iron and steel, salt solutions [2, 6] have been used for accelerating the formation of rust-like corrosion products for "plugging" voids. Corse [7] reported that alcoholic solutions of phenol-formaldehyde resin were used as sealants for aluminum crankcases during World War I and that H. W. Gillett used this resin as early as 1912 for sealing aluminum intake manifolds for automobile engines. In the case of magnesium castings, tung oil is reported [8] to be a very satisfactory sealant, but during World War II its use for this application was prohibited by the War Production Board, and consequently other sealants had to be developed. Satisfactory results were obtained on magnesium castings with mixtures of styrene with either a heavy bodied linseed oil [9] or with certain synthetic resins [10, 11].

[1] Figures in brackets indicate literature references at the end of this paper.

A satisfactory sealant should have low viscos and good wetting properties so that it can pe trate readily into small voids. It also should reasonably stable during storage in the liqu state. In curing it should form a resilient, herent solid unaffected by moderately hi temperatures and reasonably inert when expos to hot oil, gasoline, water, and other comm solvents.

Of the materials mentioned some are satisfacto as sealants in certain applications, but none them can be regarded as a universal seala Because of the many recent developments in t field of plastics, it was considered desirable investigate the effectiveness and durability sealants of a number of available liquid synth resins. The present investigation was limi to this class of materials. Experiments w made to establish the sealing efficiency of seve different resins and durability tests were co ducted on specimens treated with the most effici sealants.

II. Materials and Apparatus

The porous specimens that were used in this investigation were bushings 2 inches in outside diameter and 2 inches long, with a wall thickness of one-eighth inch. Some were cast to size and machined on the ends only. Others were cast oversize and machined inside and outside to dimensions. The materials were commercial aluminum, an alloy of copper and 3½ percent silicon, and red brass (85 percent copper and 5 percent each of lead, tin, and zinc). Some of the specimens had been prepared previously for another investigation; others were cast especially for this work with the melting and casting conditions controlled to favor the development of the desired amount of porosity. For the aluminum specimens this involved heating the metal to about 1,600° F (250° F above the normal maximum heating temperature) which tends to develop a coarse structure and also favors gas absorption. In casting the copper alloy specimens, some of the mold surfaces were moistened with kerosene to insure the development of porous castings.

The degree of porosity in each specimen was determined by a hydrostatic pressure test. S specimens showed considerable leakage at pr sures as low as 25 lb/in.^{2} and water was emitte as a steady spray when the pressure was increase to 100 lb/in^2. Others showed only slight signs leakage at 600 lb/in^2. Specimens that co withstand a pressure of 600 lb/in.^{2} for 5 minut without leaking were considered sound, and th criterion was adopted as a basis for judging t success of the sealing treatments.

Examination of sections of porous specime showed that most of the porosity was due t microshrinkage and consisted of cavities along th grain boundaries. This is illustrated by the micr graph of a polished section of a specimen of copp silicon alloy, shown in figure 1. The maximu width of cavity observed in any specimen w about 0.002 inch, but most of the cavities we much smaller.

The impregnating chamber shown in figure was constructed for impregnation of the specime by the vacuum-pressure method. The chamb consisted of a 12-inch length of 8-inch pipe, close

FIGURE 1.—*Micrograph of a section of a copper-silicon alloy casting showing microporosity; unetched;* $\times 500$.

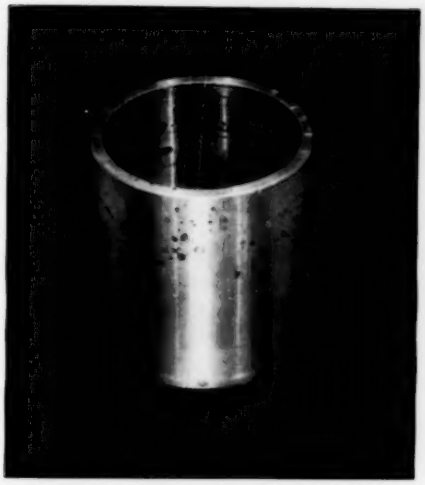

FIGURE 3.—*Porous aluminum casting showing the exudation of resin that occurred during curing.*

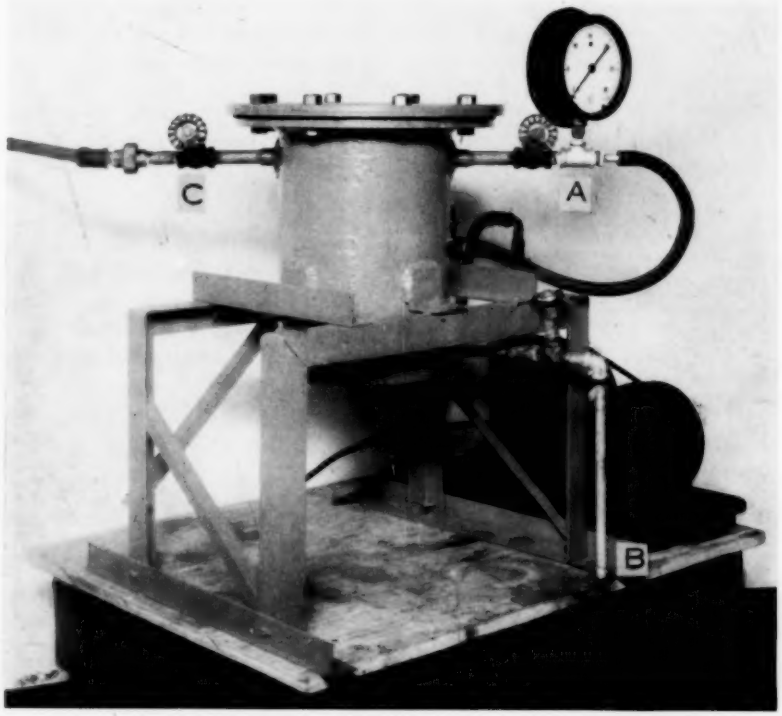

FIGURE 2.—*Impregnating chamber used in sealing porous castings.*

A, Vacuum gauge and connection to vacuum pump; *B*, inlet tube for admitting sealant; *C*, connection to supply of high-pressure air.

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t one end and provided with a flange at the top nd. The top was closed with a ½-inch steel over plate fitted with a rubber gasket and held n place by bolts. Air and vacuum connections ere welded into the side of the vessel near the op, and a connection for admitting the resin was cated near the bottom. Each of these connecions was controlled with a valve and a drainage ole in the bottom was closed with a pipe plug.

The impregnating chamber permitted treatment f 10 specimens at one time with about one-half allon of resin. The 10 specimens used for each est were selected so that specimens of reasonably mparable porosity were treated with each resin. he procedure consisted in placing the cleaned nd dried specimens in the chamber, closing all penings except the one to the vacuum pump, nd evacuating to a vacuum of 28 or 29 inches of ercury for 1 hour. Then sufficient sealant was rawn in to cover the specimens and an air pres- ure of 75 lb/in.^{2} applied for 1 hour. After the ressure was released, the sealant was withdrawn nd the specimens were allowed to drain. Most f the adhering resin was removed by wiping. A nse in a suitable solvent, followed by wiping ith a clean rag, removed the last of the sealant om the surfaces. The specimens were then cured under conditions recommended for each particular resin by the manufacturer. The curing schedules ranged from 1 hour at about 200° F to 4 hours at 275° to 350° F. In the case of many of the resins some exudation occurred during curing but the exuded material was removed before making pressure tests. The exudation that occurred during the curing of a porous aluminum specimen impregnated with a phenolic resin is shown in figure 3.

Fourteen resins were selected for investigation, representing commercially available products. Six of these have been recommended specifically as sealants; the others were selected for comparison with the commercial sealants. A low viscosity is an important requisite for sealants to insure penetration, but it is questionable whether or not this property should be gained at the expense of the solids content of a resin through dilution with volatile solvents. For most of the resins the desired viscosities were obtained by using suitable amounts of the more fluid reactants like styrene in the copolymerizing resins; a few of the resins required dilution with solvents but these additions were not made on the basis of equal fluidities. One resin, No. 3, contained no added solvent and the viscosity of this sealant was somewhat higher than for the others.

III. Results of Impregnation Tests

The results of the sealing treatments with the arious resins as indicated by pressure tests are hown in table 1. In this and in subsequent

TABLE 1.—*Results of sealing treatments with different resins as indicated by pressure tests* [a]

Type of resin	Number of porous specimens treated	Percentage of specimens sealed in—		Remarks
		1 impregnation	2 impregnations	
Styrene-polyester [b]	10	20	20	
do [b]	10	20	.....	
Phenolic [b]	13	46	46	Resin has high solids content.
Styrene-polyester [c]	12	33	66	
Polyester [c]	10	50	.....	
Unsaturated polyester [c]	10	20	30	
do [c]	10	30	.....	Resin No. 6 with wetting agent.

TABLE 1.—*Results of sealing treatments with different resins as indicated by pressure tests* [a]—Continued

Type of resin	Number of porous specimens treated	Percentage of specimens sealed in—		Remarks
		1 impregnation	2 impregnations	
8. Styrene-alkyd [c]	10	30	.....	
9. Phenol-formaldehyde. [c]	10	30	.....	Low molecular weight resin.
10. Resorcinal-formaldehyde. [c]	9	11	.....	Fast-curing resin.
11. Styrene-alkyd [c]	10	20	.....	
12. Phenolic with siliceous filler. [b]	10	10	.....	Resin contains 65% solids.
13. Phenolic [b]	38	58	79	Resin contains 52% solids.
14. Styrene-polyester [d]	36	47	86	

[a] Specimens were tested at a hydrostatic pressure of 600 lb/in.^{2} for 5 minutes.
[b] Recommended by the manufacturer for general use.
[c] Resins not marketed as sealants.
[d] Recommended by the manufacturer for aluminum or magnesium alloys.

tables, the sealants are arranged according to arbitrarily assigned numbers with the type of resin indicated. For some of the resins, data are given to show the effect of a second treatment on the specimens that had not been completely sealed in the initial treatment. Only four of the resins successfully sealed 46 percent or more of the specimens in one treatment. One of these, No. 3, showed a sealing efficiency of 46 percent in the initial treatment but indicated no improvement in the second treatment. Resin No. 5 sealed 50 percent of the test specimens in one treatment, but the curing of this resin was catalysed by contact with copper even at room temperature and the bronze specimens became coated with a solid material during impregnation, which was exceedingly difficult to remove. Two of the sealants, No. 13 and No. 14, made the best showing. No. 13 is a phenolic resin in alcohol solution and is recommended by the manufacturer for eliminating leakage in all types of metals and alloys. No. 14 is a styrene-polyester resin developed particularly for sealing aluminum and magnesium castings. In the initial treatment No. 13 sealed 58 percent of the specimens tested and No. 14 sealed 47 percent. After two treatments the total percentages sealed were 79 percent and 86 percent, respectively, for the two resins.

As these two resins were the only ones that yielded reasonably satisfactory results in the sealing treatments, durability tests were confined to specimens repaired with these sealants.

IV. Durability Tests on Sealed Specimens

Repaired castings must withstand exposure to service conditions in addition to being pressure tight immediately after the impregnation treatment. Thus it is important to know how the sealing material will withstand exposure to hot motor oil, high octane gasoline, or boiling water over extended periods. Likewise a knowledge of the effect of elevated temperatures or of hydraulic pressures in excess of 600 lb/in.^{2} may be of importance in some applications. Another factor deserving consideration is the ability of the sealed casting to withstand thermal shock.

In order to evaluate the durability of the seal produced by the two most efficient sealants, a number of experiments were conducted. In most of these tests five specimens sealed with each resin were exposed simultaneously under each condition, and the durability was judged by pressure tests on the specimens, either at regular intervals or upon completion of the exposure test.

1. Exposure to liquids

The effects of exposure to motor oil at 250° F, high octane gasoline (AN-F-28 fighter fuel) at room temperature, and boiling water were determined by completely immersing sealed specimens in each medium. The exposure tests were continued for 16 weeks, the specimens being removed for pressure tests at intervals of 4 weeks. Sound specimens were replaced for further exposure after each pressure test. The results of these tests are given in table 2.

TABLE 2.—*Results of the exposure of sealed specimens to liquids*

Sealant	Exposure medium	Number of specimens tested	Number of specimens pressure tight • after—			
			4 weeks	8 weeks	12 weeks	16 weeks
No. 13	Motor oil at 250° F	5	4	2	2	
No. 14	do	5	5	4	4	
No. 13	High-octane gasoline at room temperature	5	3	2	2	
No. 14	do	5	5	5	5	
No. 13	Boiling water	5	5	4	4	
No. 14	do	5	4	4	4	

• Pressure tested at 600 lb/in.^{2} for 5 minutes.

2. Effect of elevated temperatures

The stability of the two sealants at elevated temperatures was determined by exposing sealed specimens in air at a specified temperature for 4 hours, pressure testing the specimens, and then exposing the pressure tight specimens at a higher temperature. This procedure was continued until all of the specimens had failed. The first exposure was at 400° F and the temperature was increased by 100° F in each successive cycle. The results of the tests are given in table 3.

TABLE 3.—*Results of exposure of sealed specimens at elevated temperatures*

Sealant	Number of specimens tested	Number of specimens pressure tight[a] after 5 hours at —			
		400° F	500° F	600° F	700° F
No. 13	5	4	4	1	0
No. 14	5	3	1	0	----

[a] Pressure tested at 600 lb/in.² for 5 minutes.

TABLE 4.—*Results of tests on sealed specimens at pressures higher than 600 lb/in.²*

Sealant	Number of specimens tested	Number of specimens pressure tight after 5 minutes at—			
		700 lb/in.²	800 lb/in.²	1,000 lb/in.²	1,200 lb/in.²
No. 13	3	3	1	1	0
No. 14	4	3	0	----	----

3. Effect of testing at pressures in excess of 600 lb/in.²

Another group of castings was tested to determine the maximum pressures that the sealed specimens could withstand. The specimens were first subjected to a hydrostatic pressure of 700 lb/in.² for 5 minutes. Those specimens which were sound at this pressure were then tested at 800 lb/in.². The pressures were thus increased by increments of 100 to 200 lb/in.² until leaks developed in all of the specimens. The results of these tests are shown in table 4.

4. Effect of thermal shock and aging

The ability of the sealed castings to withstand thermal shock was determined by alternately immersing the specimens in baths at 212° and 32° F, respectively. The castings were kept in each bath until they attained the temperature of the medium. After 25 cycles (50 changes of temperature) the specimens were tested for pressure tightness. Four of the five specimens treated with resin No. 13 had developed leaks, whereas only one of the five specimens sealed with resin No. 14 had failed.

Five specimens sealed with each resin were retested for pressure tightness after storage at room temperature for 6 months. No change had occurred in any of the specimens during this period.

V. Discussion of Results and Conclusions

Of fourteen resins tested to determine their efficiency as sealants for porous castings, only two showed promise in this respect. Even these two resins sealed only 50 percent of the specimens subjected to one treatment but a second impregnation increased the sealing efficiency to about 90 percent. As a double treatment does not insure complete sealing, it is necessary to test all castings to identify those which have not been sealed. This undesirable feature necessarily limits the value of the process, and for that reason the use of sealants, except in some special applications, probably will be resorted to only in emergencies. Regardless of the circumstances requiring the use of a given sealant, its durability under service conditions should be given first consideration. The results of the tests indicated that a resin may be decidedly superior for one type of exposure but may be of questionable value under other service conditions. Thus the styrene-polyester resin (No. 14) was considerably more satisfactory than the phenolic resin (No. 13) in exposure to petroleum products (table 2), while the phenolic resin was superior for elevated temperature conditions. In addition, the phenolic resin required the application of higher pressures to produce failure at room temperatures. Both resins were reasonably stable in exposure to boiling water. Under thermal shock conditions the polyester resin (No. 14) was decidedly superior. Undoubtedly this is due to the fact that the latter forms a resilient material upon curing whereas the phenol-formaldehyde resin is converted into a glassy, brittle mass that fractures readily as the casting expands and contracts.

Although impregnation with sealants now available may be a useful method for rendering certain types of porous castings pressure tight for limited service conditions, the results of this investigation suggest that in general the production of leakproof castings remains essentially a foundry problem. Thus the development of pressure tightness in castings, in general, will result from careful design, judicious selection of alloys, and the application of good foundry practice. It is better to avoid the formation of porosity than to try to remedy it.

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Washington, May 29, 1946.

U. S. Department of Commerce
National Bureau of Standards

Research Paper RP1741
Volume 37, September 1946

Part of the Journal of Research of the National Bureau of Standards

Testing Large-Capacity Rotary Gas Meters

By Howard S. Bean, Matthew E. Benesh,[1] *and Frank C. Witting*[2]

The paper describes two methods of testing rotary gas meters of large capacity. In one method, known as the field test method, the necessary equipment is taken to the meter location. In the other method, termed the "transfer method," the test is made in a shop where conditions can be controlled more closely. Results obtained by the two methods are compared.

Tests made to study the instantaneous pressures within the closed measuring pockets of rotary meters and the effect of pulsations at the meter inlet are described, and the results discussed.

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I. Introduction

During the last 20 years the use of gas as an industrial fuel has increased many fold. As examples, many bakeries (from the small neighborhood shop to the large wholesale bakery), enamel and paint drying ovens, and heat-treating ovens for tools and machinery parts use gas as their source of heat. To measure the gas supplied to these users, a number of different types and sizes of meters have been developed. It is fortunate that this has occurred, as no one type or size possesses the necessary characteristics to fulfill satisfactorily all the conditions encountered.

The development of these meters and the increase in their unit capacity (particularly in the rotary type) introduces the problem of testing such meters. Some of the meter manufacturers have gasometer-type provers of as much as 3,000-ft.[3] capacity. The chief disadvantage of using these provers for testing some of the largest meters is that the high inertia of the moving parts of both meters and provers makes it difficult to perform tests at uniform rates of flow anywhere near the rated capacities of the meters or even their normal rates of operation. Moreover, moving some of the largest meters to a prover is so expensive as to practically prohibit routine testing of them by this method. Hence, the development of equipment and methods for testing these meters to their full capacity and for checking their condition while in service is of importance to meter manufacturers, users, and public utility commissioners.

Technical and commercial associations through appropriate committees, as well as individual companies, have given considerable attention to the metering of gas and testing of gas meters. The Bureau has cooperated in several of these efforts, as one of its functions is to assist in the development of methods of testing. The work here described was done in cooperation with the Peoples Gas Light & Coke Co., Chicago, Ill., under arrangements similar to those that applied in connection with the Joliet reference meter investigation described elsewhere.[3]

[3] H. S. Bean, M. E. Benesh, and F. C. Witting, Joliet reference gas meter, J. Research NBS 17, 207 (1936) RP908.

II. General Outline of Methods and Conclusions

1. Rotary Meters

The rotary meters referred to in this paper are the two-lobed impeller type. A cross-sectional elevation of such a meter is shown in figure 1. Air or gas flowing through the meter in the direction indicated by the broken arrows causes the impellers to rotate in the direction shown by the solid arrows. The volume of air or gas trapped within a pocket such as that formed between impeller *A* and the semicircular portion of the case *C* is discharged into the meter outlet. Four such pockets are filled and discharged during the course of each revolution. Theoretically, the two impellers, *A* and *B*, should be in continuous rolling contact with each other and continuous sliding contact with the two semicircular parts of the meter case, *C* and *D*. Under these ideal conditions, which no actual meter fulfills exactly, the volume of each pocket may be computed from the dimensions of the case and impellers, as the cross-sectional outline of each impeller is developed by geometric curves and the inside of the case is a semicircle. Therefore, the area of one meter pocket is equal to one-half the impeller section area subtracted from the area of the semicircular portion of the meter case, *C*. Multiplying this area by four and then by the impeller length gives what may be called the "dimensional" displacement per revolution.[4]

In an actual meter, the true displacement differs from the dimensional displacement defined above because it is necessary to avoid impeller wear and excessive differential pressures across the meter. To do this, there are small but significant clearances provided between the impellers and the case. Also the surfaces of the impellers are not in actual rolling contact, and the proper phase relationship between the impellers is maintained by spur gears on the impeller shafts outside the impeller chamber.

These small but necessary clearances introduce two modifications to the simple relationship

[4] In the past, one manufacturer has used this mathematical derivation of meter displacement in computing the listed displacements for his meters.

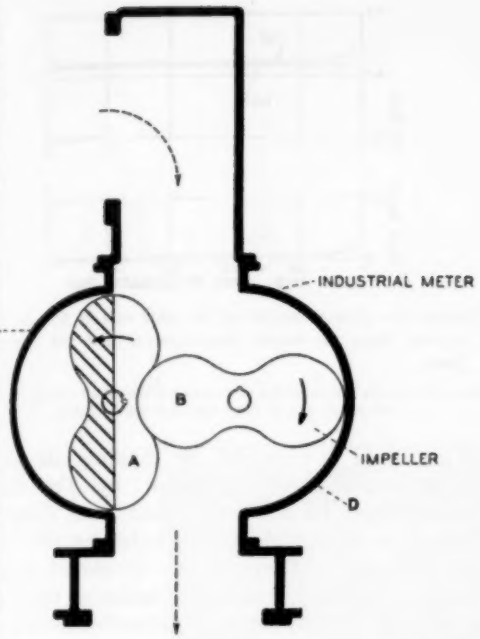

FIGURE 1.—*Cross-sectional elevation of a rotary gas meter.*
The broken arrows indicate the direction of gas flow, the solid arrows the direction of rotation of the impellers

between meter dimensions and displacement. The first is that the actual displacement per revolution differs from that computed from the actual dimensions. The second is that a small quantity of gas will pass through the clearances without affecting the meter indications. The magnitude of the first modification is a function of the meter clearances only, whereas the second, in addition to being a function of the meter clearances and the density and viscosity of the gas, is also a function of the pressure drop across the meter, which is a variable.

In order to evaluate the magnitudes of these modifications, two methods of testing rotary meters have been developed and are here described. One of these is called the "field method" because by it an industrial meter may be tested in either the meter shop or its actual service location. The other, referred to as the "transfer method", is a laboratory method and is applicable to the testing of any type of meter that operates close to atmospheric pressure and has a capacity range within that of the available testing equipment (96 to 3,000,000 ft³/hr in the present case).

The transfer method and the equipment used with it were developed first and used to test a large number of rotary meters. An analysis of the results of these tests led to the development of the field method. Representative meters, previously tested by the transfer method, were tested again by the field method to establish its reliability. The remarkable agreement between the results obtained with the two methods is illustrated by a detailed example in Section II and by other examples summarized in Section III.

2. Field method of meter calibration

The field method of meter calibration consists of three individual determinations (1) the true meter displacement, (2) the quantity of air or gas that passes through the clearances of the meter, and (3) the pressure drop across the meter at several rates of operation.

The meter displacement is determined by driving it mechanically at a very slow rate of speed (equivalent to 1 percent or less of its rated capacity), and maintaining a zero pressure difference across the impellers. The discharged air or gas is measured by a small, accurate reference meter, which in turn is calibrated by comparison with a primary standard. (In this instance the primary standard is a piston meter).[5] The result is reported in terms of cubic feet per revolution.

The measurement of the quantity of air or gas passing through the meter clearances consists of accurately determining the flow through the impeller clearances under static conditions and subsequently converting this information by means of an empirical relationship to the dynamic conditions occurring during the actual performance of a meter. Original data for this procedure are obtained from two simple tests. The first of these tests, referred to as the "clearance test," consists in accurately measuring the rate at which gas flows through the meter clearances at various specified differential pressures when the meter impellers are externally driven at a very slow and uniform rate of speed. The second is the "rate test," and consists in measuring the differential pressures across the meter while it is operating normally at various speeds throughout its operating range.

The results of the two tests are then combined to correlate the flow of gas or air through the impeller clearances with the meter speed. The method of

[5] See Sec. III, 2, (a), (2).

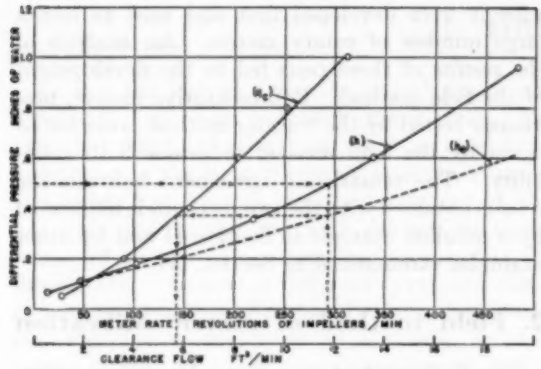

FIGURE 2.—*Curves for the relationship between meter speed· clearance flow, actual pressure drop, and effective pressure drop of a rotary gas meter.*

q_c (ft³/min) = rate of flow through the clearances.
h (in. H_2O) = actual pressure drop through the meter.
h_e (in. H_2O) = the pressure drop which is effective in producing the flow through the clearances.

doing this is illustrated in figure 2. Curve (h) is taken directly from the rate test and shows the variation of the observed differential pressure with the meter speed. Curve (h_e) is derived from (h) by an empirical relation [6] and shows the variation of the effective differential pressure with the meter speed. Curve (q_c) is taken directly from the clearance test and shows the variation of the clearance flow with the differential pressure. From these curves the clearance flow corresponding to any observed differential pressure or meter speed is obtained.

Dividing any value of the clearance flow, in cubic feet per minute by the corresponding meter speed in revolutions per minute gives the rate of flow through the clearances in cubic feet per revolution. Adding this quotient to the measured displacement per revolution gives the total rate of flow through the meter at the particular speed. The result of this operation for several different meter rates is illustrated in figure 3, in which curve (e), representing the total flow, is obtained by adding to the ordinates of curve (c), for the clearance flow, the amount of the actual displacement value (s).

The results of gas meter tests are most commonly reported by the gas industry in terms of the meter proof. It is the factor, expressed as a percentage by which the indications of a meter must be divided to obtain the true volume of gas metered. The meter proof for any particular

[6] See sec. III, 1, (c).

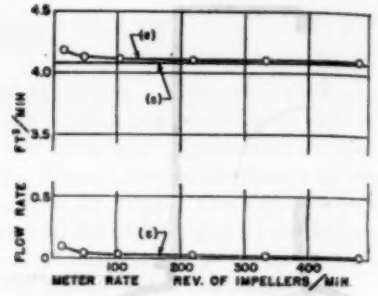

FIGURE 3.—*Determination of the total rate of flow per re olution from the actual displacement and the clearan flow.*

Line (c) is the flow through the clearances, (s) the actual displacement p revolution, and (e) is the total flow per revolution

meter speed is obtained by dividing the liste meter displacement furnished by the mete manufacturer by the value read from curve figure 3, and multiplying this value by 100. Th curve shown in figure 4 was developed in thi manner and illustrates the variation of the mete proof with the meter speed. A detailed descriptio of the equipment, procedure, and necessar computations are given in section III,1.

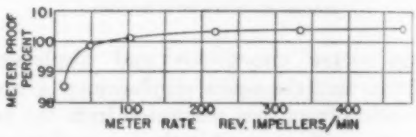

FIGURE 4.—*Proof curve of a rotary gas meter.*

This curve was developed with data from figures 2 and 3.

3. Transfer method of meter calibration

In this method, which could also be designate as one of substitution, air or gas is circulated t a desired rate of flow through the meter under te until conditions (i. e., rate, pressure, and temper ture) are constant. Then, without altering an of these conditions, the entire flow is diverte into a large storage container whose static pressur is not only very close to atmospheric pressure bu also completely independent of volume or rat of change of volume. The flow into the storag container is continued until the container i nearly full and then diverted back to the origina circulation. The time during which the flow i thus diverted or the difference in meter reading between the start and finish of the diversion an recorded as precisely as necessary. The air t

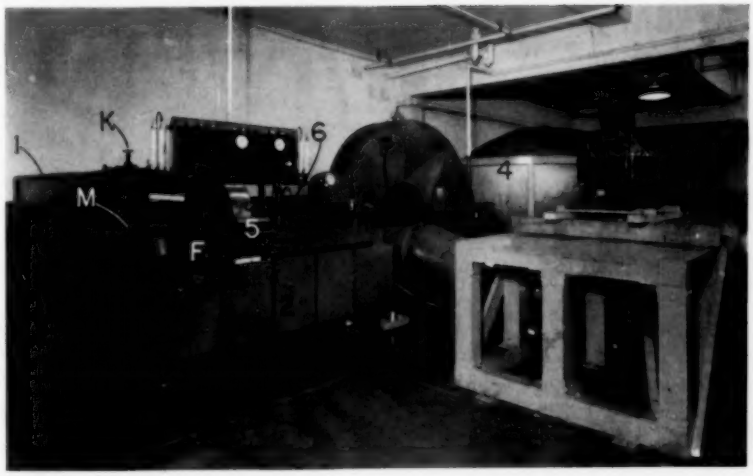

FIGURE 5.—*Transfer testing method equipment with a small rotary meter in place for testing.*

1, Housing of large secondary reference meter; 2, the heat exchanger; 3, large slide valve; 4, transfer receiver; 5, small slide valve; 6, engine. The lettered valves correspond to those of figure 17.

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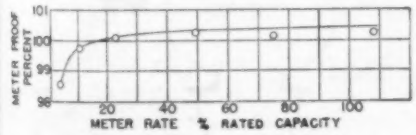
in the storage container is then measured out rough a reference meter at whatever rate is most ted to the operation of the reference meter. e pressures and temperatures of the air as it ses through the meter under test and the erence meter are measured and recorded, and se data are used to reduce the indications of the meters to a common basis for comparison.

The reference meter may be any meter of suita- capacity that has been carefully calibrated or f sufficient accuracy because of its design and de of operation (e. g., the piston meter).[7] The of of the meter under test is obtained by iding the volume indicated by it by the volume icated by the reference meter and multiplying 100.

Figure 5 shows the transfer equipment being d in testing a small rotary meter. The ailed description of the equipment, procedure necessary computations are given in section 2.

Comparison of the two test methods

The results obtained from testing a 10-in. by in. rotary meter by both methods are shown figure 6, and attention is called to the close eement between the two results. The curve he same as shown in figure 4, and was derived m the results of the field test, while the indi- ual points are the values obtained by the nsfer method. Incidentally, the two sets of ts, although made on the same meter, were ried out under very different conditions; that the transfer method being made in a special ing room under controlled conditions, whereas t by the field method was carried out in the d with part of the equipment exposed to a t snow, and with air temperatures much ow the ground (and incoming gas) temperature.



URE 6.—*Results of testing a meter by field method and transfer method.*

curve was derived from the field test method and the individual points are from the transfer method.

RP908, p. 218.

5. Summary of results and conclusions

The following is a summary of the results of tests of more than 17 rotary gas meters, ranging in capacities from 12,000 to 800,000 ft³/hr.

1. The average proof of the meters, in good mechanical condition, over the range of 5 to 150 percent of rated capacity, is between 98 and 101 percent.

2. The proof curve of any individual meter is within ±0.25 of the group average over the range of 20 to 150 percent of rated capacity, and is within ±0.5 percent of the group average over the range of 10 to 20 percent of rated capacity.

3. The size of a meter has very little influence on its proof curve when the meter speed is expressed as a percentage of the meter speed at the manufacturer's rated capacity or speed for the meter.

4. The static displacement of a rotary gas meter appears to be almost unaffected by corrosion or deposits, even those resulting from unpurified gas. Hence, having been once determined, it will seldom be necessary to be redetermined.

5. After a rotary meter has been tested once by the field method, including a hand-operated clearance test for reference, its condition at any subsequent time may be ascertained by making a simple hand-operated clearance test. If the result of this test does not differ by more than 50 percent from the original, the percentage change can be applied directly to the clearance curve and a new calibration curve developed.

6. The internal surfaces of a rotary meter can be cleaned satisfactorily, with a minimum interruption to the customer's service by several flushings of the meter with a noncorrosive solvent.

7. Pulsations, or pressure, waves created by the action of the impellers may be reflected from some part of the inlet piping so as to cause a slight irregularity in the meter proof curve. Theoretically, the maximum effect of such pulsations will occur when a single positive or negative pulse of the fundamental wave produced by a rotary meter is completely reflected and returns to the meter inlet at the exact instant to produce a maximum effect on the density of the gas about to be trapped in an impeller pocket. In these tests, the maximum reflection of pulsations was obtained with open-ended inlet pipes, and the magnitude of their effect upon the density of the

gas in the meter and the proof of the meter was about 0.6 percent.

8. The maximum effect that pulsations reflected into the meter inlet could produce upon its indication was determined by measuring the instantaneous static pressures at the meter inlet over normal operating range of meter speeds and various phase angles of the impellers. The maximum effect upon the meter proof, indicated by these measurements, amounted to about 0.8 percent, and occurred within a very narrow range of meter rates.

From the experience gained in developing these methods of testing large-capacity gas meters, and from the results of using these methods in testing rotary gas meters, as summarized above, the following conclusions have been drawn:

1. The capacity range of gas meters which may be tested by the transfer method, using the equipment herein described, is from about 95 to about 1,000,000 ft^3/hr.

2. It is believed that the results obtained by the transfer method, as used in the testing of rotary gas meters, are correct to within about ±0.
percent.

3. The field method equipment here describ
can be set up and disconnected by two men.
third man is needed only while the test is
progress.

4. The results obtained from tests of rot
gas meters by the field method are of nearly t
same degree of accuracy as those obtained by t
transfer method.

5. In general, the mechanical condition of
rotary meter can be estimated while in operati
by comparing the pressure drop across it with th
observed in the original test for the same me
speed. So long as there is no radical change
the speed–pressure-drop relation, its condition ma
be assumed to be satisfactory.

6. The effect of pulsations can be elimina
completely by the recording of the instantane
pressure within each meter pocket at the en
time the pocket is sealed off and this value used
the static pressure in the meter.

III. Detailed Description of Methods and Equipment

1. Field method of meter calibration

(a) Description of equipment

As stated in section II, the field method of testing rotary gas meters is made up of three separate tests, namely: determination of the displacement of the meter, usually referred to as the displacement test; determination of the rate of flow through the meter clearances corresponding to different pressure drops across the meter, referred to as the clearance test; and the observation of the pressure drop across the meter when it is operating at different rates is referred to as the rate test. When the second, or clearance, test is made with air an additional test is needed by which the clearance flow with gas can be calculated from the rate obtained with air, and this test is referred to as the auxiliary clearance test.

The principal items of equipment used to make these several tests, shown diagrammatically in figures 7, 8, and 9, include a small reference meter with a driving motor and gearing, a second motor and gear system for driving the industrial meter, mechanically operated breather, rubber bag differential pressure indicator, small suction-t
air blower, diaphragm-type gas meter, brake,
such additional items as thermometers, man
eters, and stop watch. A better understandi
of the testing procedure will be gained if some
these items are described in detail.

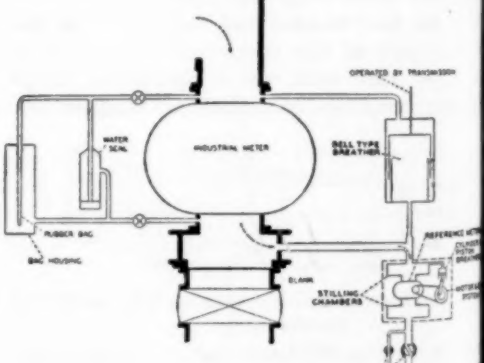
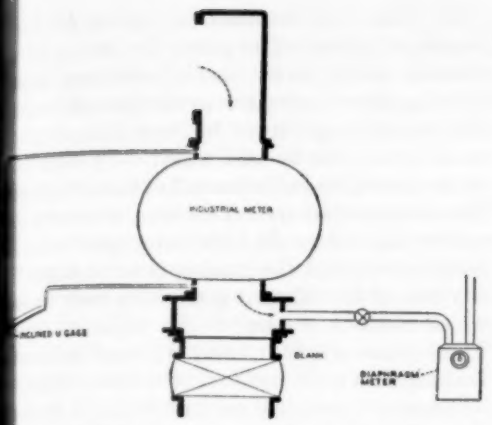


FIGURE 7.—*Diagram of the equipment and connections for the displacement test of a rotary gas meter.*



URE 8.—*Diagram of the equipment and connections for the clearance of a rotary gas meter.*

(1) *Reference meter.*—The reference meter form- a part of the equipment for the field method ts described in this paper was obtained by the dition of various special parts to a standard - by 3-in. rotary blower provided with special et and outlet flanges.[8] The conversion of a all rotary blower into a very accurate displace- nt meter is accomplished by providing the exact ount of external power necessary at all times permit the blower to operate without any flow ough its impeller clearances. The external er is supplied by a 1/20-hp induction motor ough a six-step variable-speed reducer and in-drive system. These six speeds permit the ter speed to be varied from 96 to 1,475 rpm in ps of equal geometric progression. As the ration of this type of meter tends to produce lsations, particularly in the inlet chamber, ich may affect the accuracy of the meter dications,[9] large chambers are attached to the et and outlet openings of this meter to suppress se pulsations, and as a further aid the inlet amber, which is the larger, is filled with wire th.

These chambers are suitable for the suppression high-frequency pulsations, but their capacity insufficient for the low-frequency pulsations curring during the operation of the meter at lowest meter speeds. As the suppression of low-frequency pulsations is difficult unless chambers of very large size are used, these low-frequency pulsations are eliminated at their source by the use of a compensating piston and cylinder breather. The cylinder of this breather is connected to the reference meter inlet while the piston is operated by the driving system of this meter at such a rate that it travels through four complete cycles for each revolution of the meter. A steady rate of flow of air into the meter is obtained by synchronizing the motion of this piston with the positions of the meter impellers.

Regulation of the rate of flow of air or gas through the reference meter, and therefore through the service meter under test also, is by means of the parallel connection of a 2- and a ⅜-in. plug cock attached to the reference meter outlet. The condition of zero pressure drop through the reference meter is indicated by a gage consisting of an oil bead about 1½ in. long in a slightly bowed glass tube with self-draining enlargements at each end. The number of revolutions made by the reference meter during the interval of a test is obtained from a revolution counter driven from one impeller shaft through a clutch that can be engaged or disengaged without lost motion, slippage, or overrun.

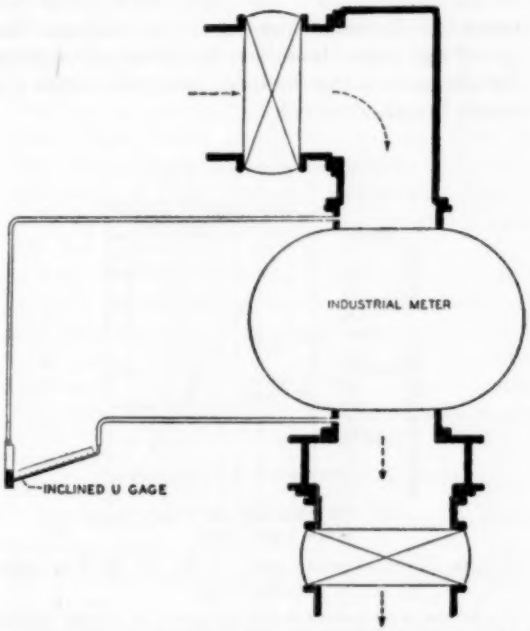


FIGURE 9.—*Equipment and connections for the rate test of a rotary gas meter.*

It is not essential that this meter be of the rotary type. Flow meters ld be used, but the calculation of the results with them would be much e tedious. Other types of displacement meters could be used if they are iciently accurate and retain their calibration within less than 0.1 percent a reasonable period of time.

See sec. IV, 2.

The reference meter, its stilling chambers, breather, gear box, and revolution counter are assembled in a common wooden case, as this not only aids in temperature control but also provides protection and greater convenience in moving. The control cocks and differential-pressure indicator are, of course, on the outside of the case. The driving motor is mounted on the top of the case so that heat from it will not affect the meter.

This assembled meter unit was calibrated by operating it in series with the piston meter, which is taken as our primary standard. The influence of pressure pulsations on the accuracy of the reference meter was checked by interposing various size cavities between the two meters. These cavities were connected to assimilate the outlet connection volumes of various sizes of industrial meters, and it was found that the calibration of the reference meter was unaffected by the size of these cavities when the meter was operated at the four highest of the six meter speeds or when the piston breather was used with the lower speed operations. In the subsequent use of the assembled reference meter unit the piston breather was used whenever the meter was operated at the three lower meter speeds.

The results of calibrating the reference meter are shown in figure 10. The upper curve gives the meter displacement per revolution without the use of the piston breather; the lower curve gives the displacement at the three lower rates when the piston breather is used.

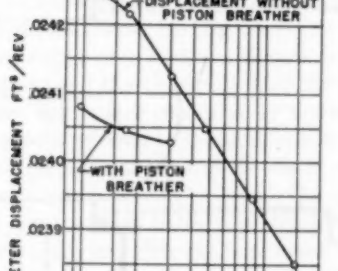


FIGURE 10.—*Calibration curves of the 2½- by 3-in. rotary reference meter.*

The addition of the breather changes the capacity or clearance volume of the system and, by making the flow through the meter steadier, decreases the flow through the clearances. Hence the difference in the calibration curves for the two conditions.

(2) *Motor and transmission system for driving industrial meters.*—The power for driving the industrial meter under test is obtained from a 1/15-hp, 110-v universal motor provided with a very sensitive governor by means of which the motor speed can be held within very close limits at any desired value between 3,000 and 7,000 rpm. The transmission system contains a series of spur gears which reduce the high motor speed to the low meter speed, and the gearing is so arranged that any one of six different gear ratios may be used which double or halve the adjacent speeds. These gears are completely enclosed in a metal housing with provision for continuous lubrication. The motor is mounted on the outside of this housing so that the two form a single piece of apparatus.

The output from this unit is suitable for driving all sizes of meters up to and including the 12- by 36-in. size. For driving the larger sizes of meters both lower speeds and greater torque are required, and these are obtained by the addition of a second gear box. The combinations of gear ratios that can be obtained in conjunction with the variations in motor speed make it possible to drive meters at speeds of less than 1/15 to over 15 rpm. When in use, the output shaft is aligned with and coupled to the meter handwheel. The weight of the unit and its reaction due to driving the meter are carried by an adjustable support bolted to the transmission housing.

(3) *Mechanical breather.*—The displacement of the industrial meter is based on the requirement that there be no appreciable pressure difference between its inlet and outlet. Also, the use of another rotary meter operated at constant speed as the reference meter for this test imposes the additional requirement that the flow reaching the reference meter shall be steady and nonpulsating. As the discharge from a rotary meter pulsates with a frequency four times the meter speed it is necessary to apply some means of neutralizing these pulsations, and this is accomplished by the combined actions of a properly synchronized mechanical breather for neutralizing the larger flow irregularities and a very lightweight breather diaphragm (the differential pressure indicator) for removing the small remaining irregularities.

Two sizes of mechanical breathers are used in this work to cover the full range of sizes of rotary displacement meter. The smaller of the breathers, used in the testing of all meters up to and including the 12- by 36-in. size, is an

cordion-type bellows mounted within a pressure vessel. One face of the bellows is fastened to the inside face of the pressure vessel. The other face is movable, with its actuating rod passing through a packing gland. The bellows are operated from a cam that is a part of the mechanical drive and transmission system, and the amplitude of the bellows movement is regulated by an adjustable linkage system between the cam and bellows. The cam rotates at four times the speed of the industrial meter and is synchronized with the meter impellers at the time of attaching the driving unit to the meter. The space within the bellows is connected to the meter inlet, and that between the bellows and pressure vessel is connected to the meter outlet.

A simple prover bell suspended by a wire and enclosed within a pressure vessel serves as the large breather. A larger size cam and linkage system is used with this breather, but otherwise the method of its connection and operation is the same as with the smaller. This breather is illustrated diagrammatically in figure 7.

(4) *Differential pressure Indicator.*—This piece of apparatus is formed by a long, wide and narrow bag of very thin rubber, suspended within a pressure chamber. The narrower sides of this chamber contain glass windows, and the bag is suspended so that when hanging freely, the narrow edges of the bag are visible through the windows. The inside of the bag is connected to the inlet side of the meter under test, and the space between the bag and the pressure chamber is connected to the meter outlet. Thus any difference between the inlet and outlet pressures will cause the bag to swell or flatten. As the force opposing any such pressure difference is due to the small horizontal component of the weight of the bag, it follows that extremely small differences of pressure will distort the bag. A continuous distortion of the bag in one direction does not mean that the pressure difference is increasing so much as it means that the direction of the difference remains unchanged. As will be mentioned later, the method of keeping the bag in its neutral, or zero, position is by regulation of the speed of the motor used to drive the industrial meter. The relatively large capacity of the chambers of this differential pressure indicator make it possible to reduce the number of speed adjustments necessary to maintain zero pressure difference. Furthermore, this large capacity assists in smoothing out any small fluctuations in the rates of flow through the industrial meter and small reference meter.

The extended range in size of the rotary meters makes it necessary to provide two sizes of differential pressure indicators, one having 10 times the volume of the other. To protect these indicators against injury from excessive pressure differences, they are provided with shallow water seals, which are part of their cases.

(5) *Small air blower, diaphragm meter, and brake.*—The small air blower is a direct-connected electrically driven blower capable of withdrawing 2,000 ft^3 of air per hour at a negative pressure of about 2 in. of water and discharging it into the atmosphere. This blower is used to draw air (or gas) through the industrial and reference meters during the displacement test.

As explained later in the description of the clearance test, a diaphragm meter is used to measure a small flow of air or gas vented from the outlet side of the industrial meter. Two sizes of ordinary diaphragm meters, of commercial design and accuracy, are required to cover the large range in sizes of rotary meters. The smaller of these two meters has a capacity of 150 ft^3/hr and is used in the testing of 10 by 30-in. and smaller rotary meters. The larger diaphragm meter has a capacity of 1,000 ft^3/hr and is used in the testing of the larger rotary meters. It is desirable that these meters be equipped with observation indexes.

The brake is a simple wooden clamp that fits over an enlargement of the extension of the impeller shaft, which is not directly driven by the motor and transmission system. The purpose of this brake is to supply sufficient braking force to take up all the backlash in both the meter gears and the gears in the driving system.

The remaining equipment required for the field method includes a stop watch, four thermometers, one vertical water manometer, one inclined water manometer, a revolution counter, and all necessary tools, pipe fittings, and rubber hose required to connect the various units to the industrial meter.

(b) Methods of conducting tests

(1) *Displacement test.*—As the displacement test is usually made with air[10] the first step is to close the inlet and outlet valves of the industrial meter,

[10] This test is not influenced by the gas composition. The line gas can be used where there is no difficulty in its disposal; however, the number of installations of this type are few.

to seal the outlet line with a blank plate,[11] and to remove a short section of the inlet piping, or to otherwise open the meter inlet to the air. The testing equipment is then connected as shown in figure 7, with the small air blower connected to the outlet to draw air through the system. The meter is then purged of the gas first by manual rotation of the impellers and then by operating the small air blower to remove any gas remaining in the system. The location of the meter handwheel is checked to see that it engages the proper impeller shaft so the driving system will rotate the meter in its normal operating direction. The driving system is coupled to and aligned with the handwheel. The cam for operating the breather is loosened and rotated until its position bears the correct phase relationship to the meter impellers and then locked in position.

The reference meter is set in a level position, its zero differential pressure indicator is adjusted so that the oil bead is centered in the bowed tube, and a water manometer is connected to measure the static pressure in the meter. The gears of the driving system for the meter are set to operate the meter at a displacement rate equal to 1 percent or less of the rated capacity of the industrial meter to be tested. To bring the system into final adjustment for a test, the cocks in the lines to the zero differential indicators of both the industrial and reference meters are closed, and the motors driving the industrial meter, the reference meter, and the blower are started simultaneously. The flow of air through the reference meter is adjusted by placing the ¾-in. cock in about midopen position and adjusting the 2-in. cock until, upon cracking the zero differential indicator cocks, the oil bead remains near the midposition. The indicator cocks are then fully opened and the zero differential pressure is maintained by constant manual adjustment of the ¾-in. valve.

Next, the rate of rotation of the industrial meter is adjusted to correspond with the rate of flow through the reference meter. To do this, the cocks to the differential indicator of the meter are cracked, and by regulation of the speed of the driving motor the meter speed is adjusted until the rubber bag remains in a neutral position. The indicator cocks are then opened wide, and the meter speed is further adjusted until the bag shows no definite tendency to swell or flatten. However, the bag will usually show a hunting, or oscillating motion, and this is reduced to a minimum by adjusting the amplitude of the mechanically operated breather.

While these adjustments are being made, as well as throughout the test, the brake installed on the industrial meter is set to maintain just enough braking force to eliminate all backlash between the meter gears and to maintain a slight load on the driving motor.

Thermometers are placed in the inlet and outlet connections of the two meters, and the equipment is ready for test as soon as the inlet and outlet temperatures of each meter agree within ±1 deg F. The rest positions of the two zero differential pressure indicators are checked, and a record of the reading of the reference meter counter is made just before a test is started. The start of a test occurs as a mark on the industrial meter handwheel passes some reference point, and the reference meter counter is started at the same instant by the engagement of its clutch. While the test is in progress one operator regulates the speed of the industrial meter and another regulates the ¾-in. cock so that zero differential pressure is maintained across each meter. A third observer reads the meter thermometers and inlet pressure every 2 min throughout a test, and keeps a record of the number of revolutions made by the industrial meter, either by direct count or by observation of the meter counter readings at the start and finish of a test. He also measures the duration of a test with a stop watch.

The usual duration of a displacement test is from 15 to 20 min. It is concluded by disengaging the reference meter index as the mark on the industrial meter handwheel again passes the reference point. The reference meter index reading is recorded, each observer is shifted to perform different duties, and a second test is made as soon as all conditions have been verified.

Upon completion of the second test the rest positions of the two zero differential gages are checked to be sure there has been no shift, and the results from the two tests are computed. The results by different observers should agree within 0.15 percent, and are computed by the equation

$$d_t = \frac{d_r N_r}{N_t} \times \frac{p_r T_t}{p_t T_r},$$

[11] If a blank plate cannot be installed in the outlet line, the line between the meter and outlet valve should be sealed with water.

which

d (ft³) = displacement per revolution
N = number of revolutions
p (in. Hg) = absolute pressure at meter inlet
T (° F) = mean of the average inlet and outlet absolute temperatures, i. e., observed temperatures +458 deg.
Subscripts i = industrial meter under test
r = reference meter.

able 1 shows the observed data and computed sult from the displacement test of the 10- by -in. meter already mentioned.

TABLE 1.—*Meter displacement test*

Meter No.: 11246 — Meter size: 10 by 30 in.
Location: Southport and Courtland. — Date: November 20, 1940.

Time intervals		Industrial meter				Reference meter			
		Index reading	Static pressure	Temperatures		Index reading	Static pressure	Temperatures	
				Inlet	Outlet			Inlet	Outlet
1		2	3	4	5	6	7	8	9
...a	sec	rev×4	in. H_2O	° F	° F	rev×1	in. H_2O	° F	° F
...	0	28, 265	0.0	.....	.....	53226.45	0.0	.....	.....
...	0	.....	.....	51.9	50.7	.....	.....	53.7	54.5
...	0	.....	.....	51.9	50.8	.....	.....	53.5	54.5
...	0	.....	.....	52.0	50.8	.....	.....	53.3	54.5
...	0	.....	.....	52.0	50.8	.....	.....	53.1	54.3
...	0	.....	.....	51.9	50.8	.....	.....	53.0	54.2
...	0	.....	.....	51.9	50.9	.....	.....	52.9	54.1
...	0	28, 387	.....	51.9	50.9	.....	.....	52.7	54.0
...	28	.....	0.0	.....	.....	58412.81	0.0	.....	.....
...olutions...		30.5	.....	.....	.....	5186.36	.....	.....	.....
...rages.....		.....	0.0	51.97	50.81	.....	0.0	53.17	54.30
				51.39		.....	.....	53.74	
...olute.....		.....	29.59	509.39		.....	29.59	511.74	

Reference meter displacement, from figure 10 for 335 rpm, $d_r = 0.024106$ ft³.

Industrial meter displacement,

$$d_i = \frac{0.024108 \times 5186.36}{30.5} \times \frac{29.59}{29.59} \times \frac{509.39}{511.74} = 4.0906$$

(2) *Clearance test.*—The purpose of this test is determine the relation between the pressure op across a meter and the rate of flow through e clearance spaces of the meter. The procedure ployed consists in developing a pressure differ- ce across the impellers by mechanically driving e meter with the outlet closed. The gas that is ereby pumped into the closed outlet chamber by the rotation of the impellers returns to the inlet chamber through the clearance spaces.

As the inner surface of a meter case is slightly uneven, the width of the clearances between the impellers and case will vary for different angular positions of the impellers. Hence in trying to maintain a constant pressure difference across the impellers, it would be necessary to vary the rate of rotation throughout each revolution, going faster as the impellers pass a wide clearance space and slower as they pass the narrower spaces. This, however, would not give a true leakage-time relation because the time interval taken to pass a given arc of narrow clearance will be longer than that taken to pass an equal arc of wide clearance. To overcome this disadvantage the meter is driven at a constant rate of rotation by the driving system used with the displacement test, and the pressure difference is maintained constant by venting a small variable flow of air or gas from the discharge chamber of the meter. This vented gas or air is metered with the diaphragm meter, and its volume reduced to the conditions (i. e., temperature and pressure) that exist within the rotary meter. The simple subtraction of this metered volume from that calculated by multiplying the meter displacement by the number of revolutions gives the clearance flow during the test period.

As the rate of flow through the clearance spaces will vary with the specific gravity (i. e., density) and viscosity of the gas, it is desirable from this standpoint to make this test with the same kind of gas that the meter is to measure. To do this, the removed section of inlet pipe is replaced, the inlet valve opened, the meter completely purged of air, and the testing equipment used with the displacement test replaced with that shown schematically in figure 8. It is noted that both breathers are removed and replaced by the inclined draft gage and the small rotary reference meter is replaced by the diaphragm meter. During a test the observed quantities are draft-gage reading, number of meter revolutions, time interval, and volume of gas vented through the diaphragm meter. Determinations of the volume of clearance flow are made at a number of different pressures covering the operating range of the meter, and the result from each is expressed in terms of cubic feet per minute by using the equation

$$q_c = \frac{(Nd - V_i)60}{t},$$

in which

q_c (ft^3) = clearance flow per minute
N = number of revolutions
d (ft^3) = displacement per revolution
V_t (ft^3) = volume of vented gas (difference of diaphragm meter readings)
t (sec) = test period.

Table 2 shows the observed data and computed results from the clearance pressure drop test of the 10- by 30-in. meter. It should be noted that these tests were made with air to facilitate the comparison of this method with the transfer method made previously with air.

TABLE 2.—*Clearance test*

Meter: 11246.
Meter size: 10 by 30 in.
Rated hourly capacity: 110,000 ft^3/hr.
Meter displacement listed by manufacturer: 4.115 ft^3.
Date: November 22, 1940.
Location: Southport & Courtland.

Differential pressure	Time interval	Volume displaced by rotation of meter	Volume through diaphragm meter	Volume through clearances, col. 3−col. 4	Rate of flow through clearances, 60×col. 5 ÷ col. 2
1	2	3	4	5	6
in. H_2O	*sec.*	ft^3	ft^3	ft^3	ft^3/*min*
0.05	92.2	4.115	2.35	1.765	1.15
.10	63.4	4.115	2.14	1.975	1.87
.10	64.0	4.116	1.93	2.185	2.05
.10	64.0	4.115	1.95	2.165	2.03
.20	54.1	4.115	0.87	3.245	3.60
.40	55.2	8.230	2.73	5.48	5.96
.40	54.9	8.230	2.57	5.66	6.19
.40	54.9	8.230	2.54	5.69	6.22
.60	53.4	12.345	5.07	7.28	8.18
.60	53.4	12.345	5.05	7.30	8.20
.80	53.4	12.345	3.44	8.90	10.00
.80	53.2	12.345	3.39	8.96	10.11
1.00	61.4	16.46	3.73	12.73	12.44
1.00	61.1	16.46	3.73	12.73	12.50

(3) *Auxiliary clearance test.*—In most installations the industrial meter is in a location where small amounts of gas discharged through the diaphragm meter cannot be vented conveniently, so the clearance test is made with air. In this case the test is performed in the manner just described, the only difference is that in setting up the equipment the inlet section of pipe is not replaced and the small blower is connected to draw air through the diaphragm meter. Afterward an auxiliary test is made to obtain the factors for computing the rates at which gas would flow through the clearances. To do this all flow through the diaphragm meter is stopped, and the differential pressure across the impellers is held constant by varying the speed of the industrial meter. This speed variation, as well as the driving force necessary to operate the meter, is obtained by the manual operation of the handwheel, and the only test equipment required is a draft gage and a stop watch. One series of tests is made with air in the meter and another series of tests is made after the meter has been reconnected and purged with gas just previous to the removal of the blank in the meter outlet for its return to service. The tests in this series are made at the same differential pressures as were recorded during the regular clearance test with air; individual conversion factors are thus obtained for each originally recorded differential pressure.

Although this procedure may not be quite as accurate as that of making the clearance test with gas, no significant differences have been noticed. On the other hand, it has the advantage that it furnishes clearance data on meters independent of the gas being metered at the time and thus facilitates the comparison of meter tests, and also provides a basis for a simple method of checking the condition of the meter in the future.

(4) *Rate test.*—This test consists of observing the differential pressure across the meter impellers corresponding to various operating rates of the meter. The differential pressure is read from the draft gage, and the rate of operation of the meter is determined with a stop watch and the direct observation of a revolution counter or tachometer.

As this test is affected by the gas composition it is always performed in the field under normal operating conditions. To place the meter under these conditions, the handwheel is disengaged, the inlet section of pipe replaced (if it was not replaced earlier), the blank or water seal in the meter outlet is removed, and all the special test equipment except the draft gage is removed. Figure 10 shows the meter connections for this operation and columns 1 and 2 of table 3 show the observed data taken during the test on the 10- by 30-meter.

It should be noted from figure 10 that the industrial meter is now connected in the line so all the gas passed through the meter goes to the user whose consumption the meter has been installed to measure. As it is desirable to vary the meter speed to cover an extended operating range it will be necessary either to have a bypass around

TABLE 3.—*Speed test and meter proof*

Meter: No. 11246
Meter size: 10 by 30 in.
Meter speed at rating: 445.5 rpm.

Date: March 24,1930.
Location: 3921 Wabash Avenue.

Meter speed	Observed differential pressure, h	Adjustment for tip velocity (4/3)h_c	Effective differential pressure, h_e	Gas flow through clearance channels, q_c		Meter displacement at—			Meter proof	Meter speed, % rated capacity
						Zero pressure difference	Observed pressure difference	Listed by manufacturer		
1	2	3	4	5	6	7	8	9	10	11
rpm	*in. H_2O*	*in. H_2O*	*in. H_2O*	*ft³/min*	*ft³/rev*	*ft³/rev*	*ft³/rev*	*ft³/rev*	*%*	*%*
14.41	0.061	0.060	0.061	1.4	0.0972	4.0806	4.1778	4.1150	98.50	3.23
48.16	.102	.093	.099	2.0	.0415	4.0806	4.1221	4.1150	99.83	10.81
102.31	.177	.016	.161	3.1	.0300	4.0806	4.1106	4.1150	100.11	22.96
219.11	.356	.072	.284	4.7	.0214	4.0806	4.1020	4.1150	100.32	49.18
333.94	.603	.168	.435	6.6	.0197	4.0806	4.1003	4.1150	100.36	74.95
481.67	.963	.349	.614	8.3	.0172	4.0806	4.0978	4.1150	100.43	108.16

meter or to arrange with the user to vary the e of consumption to suit the various rates ired in the test. In some cases the total con- ption of the user may be considerably below rated capacity of the meter, but this is not ctionable as long as the actual operating range overed during the test.

(c) Computation of the meter proof

The proof curve of a rotary industrial meter is ined from the results of the tests described ve by a combination of graphical and mathe- tical steps. The first step is to plot the results he clearance test and the rate test on a common , as illustrated by lines (h) and (q_c) of figure 2. next step is to compute and plot the values of effective pressure drop, (h_e), across the clear- e channels for the determination of the net rance flow. The reason for this step, and a er explanation of it, are briefly as follows.

When the impellers of a rotary meter are in ion, a velocity pressure is produced just ahead ch impeller tip where it is closest to the meter . Also, a negative velocity pressure is pro- d immediately behind each tip. Each of se pressures is equivalent to the velocity pres- corresponding to the tip speed of the im- ers. The combined effect of these two velocity sures tends to produce a flow of gas or air ugh the clearance space in a direction counter the flow produced by the normal differential sure across the meter. Similar velocity pres- s, acting to produce more flow in the same ction as the main gas flow through the meter, produced at the so-called contact line between two impellers. However, the differences between the velocities of the impeller surfaces at this line are lower than those between the impeller tips and case. Similar velocity pressures are produced between the ends of the impellers and meter case, but again the average velocity difference between the two surfaces is less, and in addition the length of these clearance channels is much greater.

An analysis of the probable effects of these velocity pressures together with studies of the results of numerous meter tests indicated that their combined effects are very nearly equal to the pressure required to produce a gas velocity equal to 4/3 the velocity of the impeller tips. The effective pressure drop (h_e) is evaluated by the empirical equation.

$$h_e(\text{in. } H_2O) = h - (4/3)h_c, \qquad (1)$$

in which

h(in. H_2O) = total observed pressure drop across the meter corresponding to a particular meter speed

h_e(in. H_2O) = velocity pressure corresponding to the tangential velocity of the impeller tips.

The value of h_c is computed as follows: Let

D (in.) = maximum diameter of the meter impellers

N (rpm) = meter speed

G (ratio) = specific gravity of the gas, air = 1

v (ft/sec) = velocity, and using

0.075 (lb/ft³) = average density of air at meter

62.34 (lb/ft³) = average density of water in manometer

32.17 (ft/sec²) = acceleration of gravity.

Then

$$h_c=\frac{v^2}{2g}=\left[\frac{ND\pi}{(12)(60)}\right]^2\left[\frac{(0.075)(12)(G)}{(2)(32.17)(62.34)}\right] \quad (2)$$
$$=4.27G(ND)^2\times10^{-9}.$$

Columns 3 and 4 of table 3 show values of $(4/3)h_c$ and (h_e) computed for the 10- by 30-in. meter, and the values of (h_e) plotted against revolutions per minute are shown by the dotted line in figure 2.

The third step in the computations is to obtain values of the net clearance flow by means of the three curves of figure 2, corresponding to each observed value of the pressure drop (h), column 2, table 3. This is done by starting on line (h) with one of the values from column 2, moving vertically down to the line (h_e), then horizontally to the left to the intersection with the line (q_c), and vertically down to the clearance flow scale to read the net value of (q_c). This is recorded in column 5 of table 3.

The fourth step is to divide the values of (q_c) in column 5 by the corresponding values of N, column 1, thus giving values of the clearance flow per revolution. These values are then added to the static meter displacement obtained from the displacement test, thus giving the dynamic displacement per revolution, column 8.

The results of gas-meter tests are commonly reported by what is known as the proof of the meter. It is the factor, expressed as a percentage, by which the indications of a meter must be divided in order to obtain the true volume of gas metered. Hence, the fifth step is to compute the values of the meter proof by dividing 100 times the listed meter displacement, as given by the manufacturer, by the several values in column 8 and listing the results in column 10.

These computations are all that are needed as far as any individual meter is concerned. However, in order to be able to compare the proof curves of meters of different design and size, it is desirable to refer them to a common basis. Such a basis is obtained by expressing the meter speed as a percentage of the meter speed at rated capacity. The speed at rated capacity is obtained by dividing the rated capacity of the meter, as given by the manufacturer (usually in ft^3/hr), by 60 times the listed displacement. Hence, the sixth and last step in the computation is to divide 100 times the meter speeds of column 1 by the rated capacity speed and listing the results in column 11. The result of plotting the values in column 10 against those of column 11 is shown the curve of figure 6.

2. Transfer method of meter calibration

(a) Description of equipment

In this method the flow of air through the me under test is discharged into a suitable contain The time interval of filling the container or t meter readings at the start and end are record The air in the container is then measured through calibrated meters. The indications the meters are then referred to a common dens basis for use in the computation of the proof the first meter. The principal items of equipme for this method are the transfer container, reference meters for measuring the air out of container, and the blowers for circulating the Other items of equipment, which contribute the smoothness of operation and accuracy of sults, are the slide valves and heat exchanger the air ducts and the electric-spark revolut recorders on the meters. A description of equipment, the method of conducting a test, making the necessary computations follows.

(1) *Transfer container.*—The transfer conta used in this method is a collapsible rubber fabric bag with a maximum capacity of a 2,500 ft^3. When this bag is inflated it takes shape of a cylinder with hemispherical ends. is mounted with the axis of the cylinder horizo and supported at the maximum horizontal cr section by a wooden frame. To aid in the main nance of a uniform pressure within the bag dur inflation and exhaustion, especially at the start the inflation period and end of the exhaust period, small counterweights are attached strings leading over pulleys to tabs along the of the bag. By this means the pressure in bag is maintained at all times, at about 0.05 of water above the atmospheric pressure, wh facilitates the final evacuation of the bag.

(2) *Primary reference meter.*—The primary erence meter is the same piston meter used a part of the Joliet reference gas meter described Bureau Research Paper 908. This meter, removal from Joliet to its present location, w opened and carefully inspected, and, upon be reassembled, a few minor changes were made improve its operation at or close to atmosphe pressure. The oil sump was enlarged and

acuum system added to assist in the removal of ir pockets from the hydraulic system and to aid the drainage of oil from the chambers for the ollection of internal oil leakage. Electric sole-oids were provided for operating the fourway oil ock and an electric recording unit was added to ount and record piston strokes. The heat ex-hanger on the inlet line was enlarged, a new ater-spray system was installed, and the entire eter was enclosed in a galvanized sheet-iron ousing.

(3) *Secondary reference meters.*—The larger sec-ndary reference meter is a 6- by 18-in. rotary eter particularly machined to permit it to operate t speeds up to 2,000 rpm, which is about three mes the rated speed of a commercial meter of this ze. The meter is fitted with special inlet and utlet connections to improve its calibration char-cteristics and to minimize the pressure drop when he meter is operated at high speeds. To aid in egulating its temperature, the meter and inlet nd outlet connections are enclosed in a sheet-etal housing and sprayed with water drawn from storage basin forming its base. This storage asin is supplied with both hot and cold water so hat the temperature of the circulating water, hich determines the temperature of the meter, an be adjusted to any desired value. The housing f this meter is shown at the extreme left in figure 5.

The smaller secondary reference meter is a -C tin-case diaphragm meter, and it is used to ithdraw the final volume of air from the bag, ecause a rotary displacement meter is not suited r such low and nonuniform rates of flow. This eter is also used to introduce an initial volume f air into the transfer container to lift the top of he bag away from the duct opening. Therefore, is so arranged that air can be metered through it n either direction.

(4) *Heat exchanger.*—The heat exchanger shown n the foreground of figure 5 forms a part of the nlet duct to the large secondary reference meter. The purpose of it is to bring the temperature of he air entering the secondary reference meter to hat of the meter. This heat exchanger, through hich is circulated the same water that is used to pray the meter, was designed to reduce the tem-erature difference between the outlet air and nlet water to 0.1 deg F when the initial difference etween the inlet air and outlet water is 30 deg F.

(5) *Air blowers.*—Two blowers of a type com-monly used in ventilating work are used to circu-late the air through the ducts connecting the meter under test, the storage bag and the reference meters. Their cases were made tight by welding, and leakage around the shafts is prevented by special packing glands into which oil is fed under a pressure greater than that of the air on either side. The large blower, when operated at 1,740 rpm, is rated to deliver 16,000 ft^3/min against a back pressure of 9 in. of water. The small blower is rated to deliver 1,600 ft^3/min against the same back pressure when operated at a speed of 1,800 rpm.

(6) *Prime mover.*—The prime mover furnishing all the power required to operate the blowers and auxiliary equipment is a stock automobile engine equipped with a governor for automatic maintenance of constant speed. Although an electric motor would doubtless serve the purpose as well or better, the engine was selected because originally it was planned to have the equipment portable and independent of the availability of electric power.

(7) *Shutter valves.*— The shutter valves for diverting the air flow in and out of the transfer bag were designed to operate without displacing any air from one passage into another. As the further operating requirements to be fulfilled by the larger valve are more exacting, the construction and operation of this valve will be described in greater detail. The major operating requirements are a large port area, no leakage, no air displacement during motion, and a very short time of travel—a small fraction of a second. Studies of the possible valve designs to meet these conditions led to the development of a shutter or slide valve constructed entirely of standard cold-rolled steel members.

The seat and valve cover are made from milled sections of cold-rolled steel fastened together to form a grilled framework supporting the valve slide. When assembled the seat is mounted on a 2- by 3-ft rectangular frame with a central partition bisecting the two shorter sides to form the beginning of the dividing wall between the two outlet ducts. Oil grooves in both seat and cover completely encircle the openings, and oil under a slightly higher pressure than the air on either side of the valve is fed into these grooves to seal the valve. These grooves are covered at all times by the valve slide or by narrow spring-operated bars that slide over and cover the grooves whenever they are uncovered by the movement of the main slide plate. Figure 11 shows a vertical section

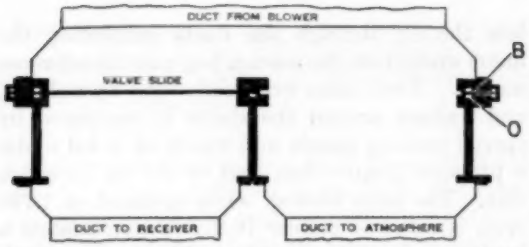


FIGURE 11.—*Longitudinal section through large shutter valve, showing relation of valve slide, oil grooves, and oil groove covering bars.*

through the valve and illustrates the location of the oil grooves and sliding bars when the valve slide is in one of its two rest positions.

The valve slide, or plate, is a single piece of ⅛-in. flat, cold-rolled steel plate, about 15 by 38 in. It moves in a direction parallel to the short dimension, and the relation of its width to that of the valve seat is such that, as it starts to close one port, it simultaneously starts to open the other. Thus the total area of open passage through the valve remains constant. Motion of the valve is obtained from three oil cylinders and pistons connected to the center and ends of the slide.

The oil cylinders, connections, and supports are designed for an operating oil pressure of 500 lb/in^2. With this pressure, the force transmitted by each piston rod is 750 lb. and the mounting for the cylinders and valve frame is such that the application of the total combined force of 2,250 lb. on the valve slide does not cause any deflection in the valve slide, seat, or cover, in excess of 0.002 in.

A cross section of one of the oil cylinders is illustrated in figure 12. The cylinders are double-acting, with the piston rods extending through bearings in both ends to insure that the actuating forces in the two directions are equal. The piston rods are square, to facilitate adjusting for clearance changes and heavy enough to withstand the full operating force in both tension and compression.

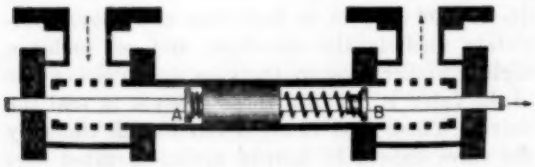


FIGURE 12.—*Longitudinal section of a cylinder, showing the outlet ports which are closed by the piston, thereby decelerating it.*

The main purpose of this particular oil cylinde design is to assure a very short time of valve trav by providing for maximum acceleration at th start of the valve movement and a controll deceleration at the end. The two plungers, *A* an *B*, on opposite sides of the piston are free to sli on the piston rod, and when unrestrained th springs cause them to assume a position about in. from the ends of the piston. The illustratio shows plunger *B* in about this position, with th piston moving from left to right. As the piste nears the end of its stroke, plunger *B* closes th exit oil port at the end of the cylinder and caus all the remaining oil to be discharged throug ports in the side of the cylinder. These side di charge ports are closed by the piston during th final 2 in. of valve travel, and are shaped to give uniform deceleration to the valve. At the end the valve movement the end of the piston is flu with the inside face of the plunger *B*, and plunge *A* is being separated from the piston by its sprin This separation is completed before the valv moves in the opposite direction, as it takes but few seconds, a time interval which is always le than that between successive movements of th valve. To start motion in the opposite directio oil is introduced through the large port at the en of the cylinder, and as the piston moves throug the first 2 in. of its stroke, additional oil ports a opened. Figure 13 shows the valve in cou of construction.

The oil for operating the pistons is circulate by a high-pressure gear pump, and its flow to an from the cylinders is controlled by a four-way plu cock. Particular attention was given to the de sign of this cock to assure a very smooth actio The core of the cock is suspended in the body b two double-row precision-ground ball bearing When fully open in either direction the area o the oil passage through the cock is equal to th combined area of the three oil pistons. Rotatin the core of the cock through 90° diverts the high pressure oil from one end of the cylinders to th other, and at the same time permits oil from th discharging ends of the cylinders to flow back to the oil sump.

Two steel bottles, each of about 100-in.^{3} ca pacity, are mounted in parallel above the four-way cock and serve as accumulators or reservoirs for high-pressure oil. When the shutter valve i ready for operation about 40 percent of the volume of these accumulators is filled with carbon

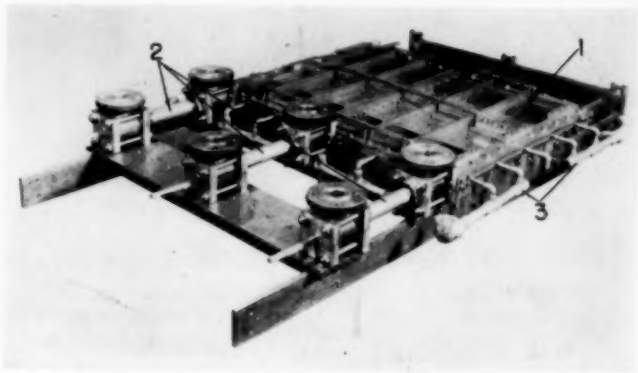


FIGURE 13.—*Large slide valve nearly ready for installation, viewed from the top or inlet side.*

Valve slide, 1, is in midposition; the operating cylinders, 2, with their pistons have been mounted; and one oil distribution header, 3, supplying the sealing oil grooves is nearly completed.

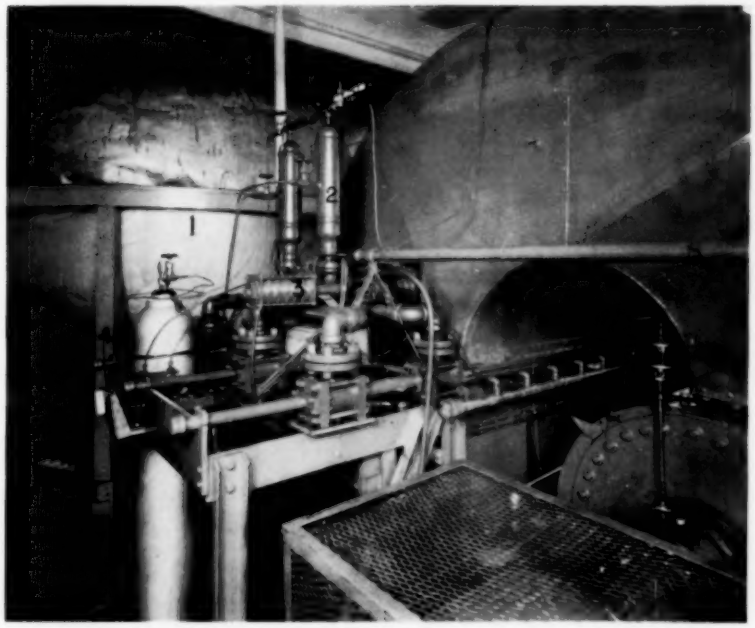


FIGURE 15.—*Completed assembly of large slide valve.*
1, Transfer receiver; 2, accumulators; 3, solonoid for the large four-way oil valve; 4, microswitch in series with industrial meter recorder.

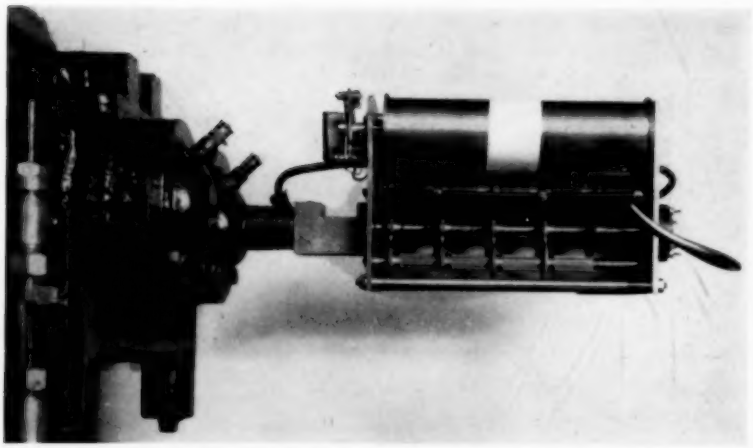
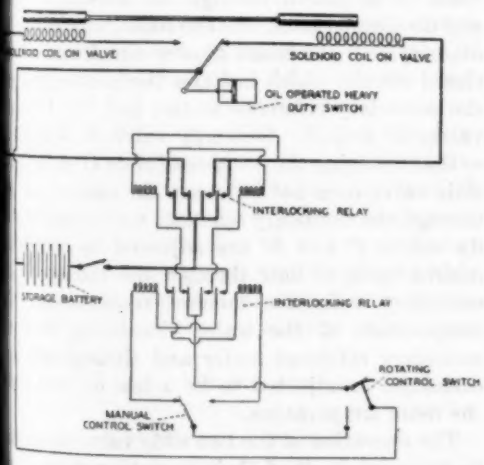


FIGURE 16.—*Jump-spark revolution counter attached to a rotary gas meter.*
In an actual test, the width of the paper used is equal to the full length of the roll.

oxide from high-pressure storage. When the r-way cock is rotated the carbon dioxide, expanding, causes the rate of oil flow into cylinders to be greatly in excess of the pump tput, thus effecting very rapid operation of valve slide. By this expansion and ejection oil the pressure in the accumulators drops about percent, and it requires about 8 seconds for the mp to refill the accumulators and restore the ginal pressure. This pressure may be main-ned at any desired value up to 500 lb/in.^{2} by adjustment of a relief valve on the pump dis-rge. This method of supplying power for the e movement, together with the shape of the inder ports, provides a very rapid acceleration d controlled deceleration.

Two large electric solenoids, each capable of rting a pull of about 40 lb through a distance of n. are used to rotate the core of the four-way k. The current for these solenoids is obtained m two 6-volt storage batteries connected in es and controlled by two switches that are erlocked by a system of relays. The first of se is a double-throw toggle switch, and the side which it is thrown determines which solenoid to be energized and thus the direction in which shutter valve will move. The second is a ating switch driven by the meter being tested, ich insures that the meter impellers are always the same position when the valve slide starts move in either direction. The electric circuit d to accomplish this result is shown in figure 14.



URE 14.—*Diagram of circuits for controlling operation of large slide valve.*

The solenoid circuits are automatically opened by an oil-operated, heavy-duty snap-acting knife switch a fifth of a second after the movement of the four-way cock so as to avoid having the relay contacts open under the heavy current (100 amperes or more). Also all other electric circuits controlling the energizing of the solenoid circuits are automatically opened immediately after their respective relays have completed their individual movements and are not energized again until the start of the next movement. The short time the various electric circuits are energized permits the use of very heavy currents in order to obtain maximum speed of action without danger of overheating the relays or solenoids. Figure 15 shows the valve in its actual service location, the entrance and exit ducts, the oil headers for sealing the valve, the hydraulic cylinders, the accumulating bottles, the four-way cock, and the two electric solenoids.

The small shutter valve is similar to the large one, but it is much simpler because of its smaller size and the fact that the time interval between successive valve movements can be measured in minutes rather than seconds. The valve seat and cover are each made from a single piece of flat cold-rolled steel 3/4 in. thick with ports and oil grooves milled out. The valve slide is a single piece of 1/8-in. cold-rolled steel plate with the piston rods attached to extensions at the four corners and operated by two double-acting cylinders. These two oil cylinders with their pistons are designed to control the acceleration and deceleration like those for the large valve, but the design is not as elaborate because the mass and required speed of the valve slide are much less than those of the larger valve. A simple 1/4-in. four-way cock operated by a pair of solenoids is used to control the operation of this small shutter valve. The same type of relay control system is used, with the rotary switch being operated by the secondary reference meter. The high-pressure oil line to the four-way valve is taken directly from the oil-pump discharge that connects it indirectly to the two high-pressure accumulators of the large shutter valve. The total port area of this small valve is about 20 in.^{2}, and the stroke of the valve slide is about 3¼ in. This small shutter valve with its inlet, its two outlet ducts, and its oil reservoir are visible just above the heat exchanger in the foreground of figure 5.

(8) *Revolution recorders.*—It has been mentioned previously that it is necessary to start and finish

the test of a rotary meter without any change in the meter speed, so it is necessary that the meter reading at the start and finish be taken while the meter is in operation. As it is impossible to read by eye the index of any operating meter at the exact instant of the beginning or ending of a test, a form of electric recording index was developed that is attached to both the reference meter and the meter under test. Figure 16 shows one of these recorders, which has a series of five rotating helices geared together so a 10-to-1 relation exists between revolutions of successive helices. Each helix is formed by winding Nichrome wire in a helical groove cut in a Bakelite spool with a uniform advance of 1 in./revolution. In attaching the recorder to the meter, the first helix is connected directly to the regular meter index shaft; in the case of a rotary meter this is an extension of one of the impeller shafts.

The record is obtained by causing an electric spark to pass from each helix wire through a sheet of paper to the sharpened edges of stationary stainless-steel strips mounted parallel to the axes of the helices. The gap between the metal strips and the helical wires is just enough to pass a sheet of writing paper freely. The electric sparks burn small holes in the paper, thus locating and recording the exact positions of each helix at the instant of current flow. The paper is advanced automatically after each record, and at the end of a test it is removed and placed on a transparency frame, where the spark record is read with the aid of a suitable scale.

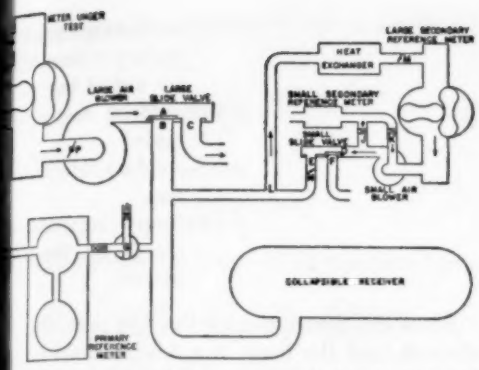
Two ordinary automobile engine ignition coils are used with each recorder to supply the high-voltage current. The secondary, or high-tension, winding of one coil is connected to the first two helices, which are series connected, while the secondary of the other coil is connected to the remaining three helices, which are also series connected. Each of the primary windings of the two coils are connected in series to make and break switches and a source of current—dry cells in this case. Two such switches are used with each of the recorders for the meter under test and the secondary reference meter; those of the former are mounted on the large shutter valve and those of the latter on the small shutter valve. These switches are three-way microswitches, with condensers connected across the switch points, and mounted so one is operated as the shutter starts moving and the other is operated as the shutter completes its movement. In this manner the time of motion of the large shutter valve is recorded in terms of the movement of the meter under test and the time of motion of the small shutter valve is recorded in terms of the movement of the secondary reference meter.

Similar jump-spark recorders are used with the piston meter and the small secondary reference meter, but these meters are stationary when the recordings are made, so the operation of the primary circuit make-and-break switches and the advancement of the paper are done by hand. A smaller operating range is required with these two meters, so four instead of five helices are used. Also, as the function of the piston meter recorder is to count the number of piston strokes and not revolutions, a solenoid operated ratchet is used to advance the first helix one-tenth turn for each stroke.

(b) Method of Conducting Tests

(1) *Testing of industrial meters.*—To test an industrial meter, such as a rotary meter, the outlet of the meter is connected to the suction side of a large blower, as shown in figure 17. The recorder is connected to the meter index shaft or an end of one impeller shaft, and other test equipment such as thermometers and pressure gages are installed. With the shutter valves in the positions shown in figure 17, the engine and blowers are started and brought up to the desired speed. In one system this causes air from the room to be drawn through the industrial meter and discharged back into the room, whereas in the other system the small blower circulates air in a closed circuit, which includes the heat exchanger, the secondary reference meter, and the butterfly valves M and N. Butterfly valve N is adjusted so that changing the position of slide D of the small slide valve does not influence the rate of air flow through the secondary reference meter, and butterfly valves P and M are adjusted to obtain the desired rates of flow through the industrial and secondary reference meters, respectively. The temperature of the water circulating over the secondary reference meter and through the heat exchanger is adjusted to be a few degrees above the room temperature.

The operation of the two slide valves is checked to assure that all of their operating elements are functioning properly. The small slide valve is left in the position where air flowing through



RE 17.—*Diagram of the arrangement of equipment used the transfer method of testing large-capacity gas ters.*

ndary reference meter is discharged into out- air until practically all the air in the bag has withdrawn and is then returned to the posi- shown in figure 17.

efore starting a test all remaining air must be oved from the bag. This is done by adjusting e *N* to produce a back pressure on the blower harge of about 2.5 in. of water above atmos- ic pressure, and then valve *J* is opened, which its air from the bag to be discharged through mall secondary reference meter to the outside. e last of the air is withdrawn from the bag the sure at the blower outlet drops to atmospheric sure, while at the blower inlet the pressure s to 2.5 in. of water below atmospheric pres- . Operation of the equipment under these itions is continued until successive spark ds spaced 5 min. apart show a change of r reading of less than 0.2 ft,[3] as it has been d that this provides a reproducible criterion mplete evacuation of the air from the bag. it provides a very good check against leak- because if there is any leakage sufficient to t the results adversely, it will not be possible duce the rate of outflow to as low a value as . The last spark record made while evacuat- he bag also becomes the first record for the which can be started as soon as valve *J* has closed.

e first step in the test procedure is to measure all amount of air into the bag to separate the and bottom surfaces. This is done in order the bag can receive a large and suddenly ted flow of air into it without injury and out causing any appreciable resistance to this air flow. To accomplish this, valve *K* is opened a predetermined amount and butterfly valve *N* is changed back to its original setting. This draws air from the room through the small secondary reference meter and discharges it into the bag at a rate of about 10 ft³/min. At the end of 5 min valve *K* is closed and a record of the index of the meter is made with the jump-spark recorder. The temperature of the air flowing through the meter is recorded every minute during this introduction period, and the average of these temperatures is taken as the meter temperature and used as such in the computations.

The second step in the test procedure comprises the main portion of the test, wherein air measured by the industrial meter being tested is discharged into the transfer bag. As this meter has been operating at the desired rate during all the preparation period so that it should have reached a condition of temperature equilibrium with the air of the room, we proceed by closing the switch, which will shift slide *A* of the large shutter valve. This closes duct *C* and opens duct *B*, causing the air flowing through the meter to be discharged into the transfer bag. When the bag is nearly full, the slide *A* is returned to its starting position. During each movement of the valve slide two records are made on the jump-spark recorder. The difference between the means of each pair of records [12] represents the number of revolutions the industrial meter has made while it was discharging air into the bag, and the difference between the two records of a single pair represents the number of revolutions the meter has made while the valve slide was shifting positions. Other data that are recorded at frequent intervals during this portion of the test procedure include the air temperature at both inlet and outlet of the meter, pressure drop through the meter, gage pressure at the meter inlet, and various operating readings that show the functioning of the meter-testing equipment but are not needed in the computations.

The next step is to measure the air out of the bag through the secondary reference meters. As the larger reference meter has been in operation for considerable time and has reached equilibrium condition, this step is started by the movement of

[12] The mean value was used to reduce the effects of any variations in rate of valve travel. However, as the rate of valve travel proved to be very uniform, the use of either set of extremes would not change the test results appreciably.

slide D of the small shutter valve to close port E and open port F. With this change, air is drawn from the bag, through the heat exchanger, through the secondary reference meter, and discharged into the room. It normally requires 6 to 7 min for this operation, and during this time the static pressure, pressure drop through meter, and both inlet and outlet meter temperatures are recorded every minute. Just before the bag is completely deflated the small shutter valve slide D is moved back to its starting position. The same type and number of jump-spark records are made with each movement of this small shutter valve as were made with the large shutter valve; thus a record of the speed of the valve action and number of revolutions made by the secondary reference meter is obtained.

The final step is to complete the evacuation of the bag, metering it out through the small secondary reference meter in the manner already described, with the exception that in this case the temperature of the air entering the meter is read every minute.

(2) *Computations of test results.*—To illustrate the computations involved in these tests, the following symbols will be used:

C (ratio)=Coefficient or correction factor of the meter under test

d (ft ^{3})=Displacement per cycle or per revolution

M (lb)=Total mass of air passed through the meter

n=Number of cycles or revolutions made by the meter

P (percent)="Proof" of meter under test

p (in. Hg. at 32° F)=Average absolute static pressure of air at meter inlet

T' (°F)=Average temperature of air flowing through meter

ρ (lb/ft ^{3})=Density of the air

Subscripts a=Flow through small secondary reference meter (i. e., the diaphragm meter) into bag

b=Flow through small secondary reference meter out of bag

c=Industrial meter being tested

s=Secondary reference meter

p=Primary reference meter (i. e., the piston meter).

From the description of the test procedure it is obvious that the mass of air introduced into the bag is equal to the mass of air withdrawn from the bag, providing there has been no leakage or condensation of any moisture in the introduced air. It should be noted that the test procedure includes a test for leakage and also that the temperatures of the secondary reference meters are maintained slightly higher than that of the room. The bag is also exercised to prevent any condensation of moisture within the bag. Under these conditions the following equations apply:

$$M_a+M_c=M_s+M_b$$

or

$$M_c=M_s+M_b-M_a$$

also

$$\left.\begin{aligned} M_a&=\rho_a\times d_a\times n_a\\ M_c&=\rho_c\times d_c\times n_c\times C_c\\ M_s&=\rho_s\times d_s\times n_s\\ M_b&=\rho_b\times d_b\times n_b \end{aligned}\right\}.$$

The density ρ may be computed by [13]

$$\rho=\frac{(1.3225)(p-0.378e)}{458+T'},$$

in which e (in. Hg at 32° F) is the partial pressure of water vapor in air. This equation can be arranged to the following:

$$\rho=\frac{(1.3225)\left(1-\frac{0.378e}{p}\right)p}{458+T'}.$$

As the equipment is operated to assure the absence of water-vapor condensation in any of the metering systems, the percentage of water vapor in the air flowing through each of the four meters remains constant. The factor $0.378e/p$ is directly proportional to the water-vapor percentage, and becomes a constant and may be combined

[13] See equation 7, BS J. Research **7**, 118 (1931) RP335.

er constants in equation 9, into a single con-
nt

$$K=1.3225\left(1-\frac{0.378e}{p}\right) \tag{10}$$

d thus

$$\rho=K\left(\frac{p}{458+T'}\right). \tag{11}$$

Applying equations 7 and 11 to equation 6 gives

$$\frac{p_c d_c n_c C_c}{458+T'_c}=\frac{Kp_s d_s n_s}{458+T'_s}+\frac{Kp_b d_b n_b}{458+T'_b}-\frac{Kp_a d_a n_a}{458+T'_a}, \tag{12}$$

ich may be reduced to the following:

$$\frac{p_c d_c n_c C_c}{458+T'_c}=\frac{p_s d_s n_s}{458+T'_s}+\frac{p_b d_b n_b}{458+T'_b}-\frac{p_a d_a n_a}{458+T'_a}. \tag{13}$$

e correction factor for the industrial meter is

$$C_c=\frac{\frac{p_s d_s n_s}{458+T'_s}+\frac{p_b d_b n_b}{458+T'_b}-\frac{p_a d_a n_a}{458+T'_a}}{\frac{p_c d_c n_c}{458+T'_c}}. \tag{14}$$

o conform with the general practice in the gas
stry, the results of meter tests are presented
"percent meter proof." The relation between
meter proof and the correction factor is

$$P_c=\frac{100}{C_c}, \tag{15}$$

by applying this to equation 14, we have

$$P_c=\frac{\frac{p_c d_c n_c}{458+T'_c}\times 100}{\frac{p_s d_s n_s}{458+T'_s}+\frac{p_b d_b n_b}{458+T'_b}-\frac{p_a d_a n_a}{458+T'_a}}. \tag{16}$$

quation 16 is the formula which could be used
alculate the "percent meter proof" of the in-
rial meter if neither of the reference meters
ired calibration. Actually these reference
ers require periodic calibration to determine
r correction factors. By the use of these
ection factors, equation 16 becomes

$$P_c=\frac{\frac{p_c d_c n_c}{458+T'_c}\times 100}{\frac{p_s d_s n_s C_s}{458+T'_s}+\frac{p_b d_b n_b C_b}{458+T'_b}-\frac{p_a d_a n_a C_a}{458+T'_a}}, \tag{17}$$

ch is the equation used to compute the proof of
eter tested by this method. It should be noted that the formula not only includes a correction factor for the larger reference meter but also includes two separate correction factors for the diaphragm reference meter, one factor for the meter operating in one direction, the other factor for the meter operating in the reverse direction. The results of some of the many tests on industrial meters are shown in section III, 3.

(3) *Calibration of secondary reference meters.*—The two reference meters are calibrated against the piston meter without removing either from their operating locations. This is done by measuring air into the bag through the piston meter and withdrawing it through one or both of the reference meters. As the final evacuation of the bag is always made through the diaphragm meter, the correction factor for this meter when measuring air out of the bag must be used with all calibrations. The correction factor for this diaphragm meter measuring air into the bag is obtained by comparing its indication after a volume of air has been measured into the bag with its corrected indication on measuring the same air out of the bag.

In the process of determining the correction factor of the larger reference meter it is not necessary to start the inflation of the bag through the diaphragm meter because the operating rate of the piston meter is low enough that the discharge from it can be diverted into the completely collapsed bag without affecting the pressure equilibrium conditions of the meter. As in the testing of an industrial meter, most of the air is withdrawn through the larger reference meter, and the final evacuation is completed through the diaphragm meter. Thus the determination of the correction factor for the larger reference meter involves the use of that for the diaphragm meter. This, however, is not objectionable, because even a rather large uncertainty in the latter would have no significant effect on the former, since the volume metered by the diaphragm meter is only 2 to 4 percent of the total volume of over 2,000 ft^3 in the bag.

(c) Discussion of some of the special features of the equipment and operating procedures

One of the most important features of this equipment is the use of the jump-spark recorders. These recorders eliminate personal errors in the reading of the meters and provide permanent records of the meter readings. Also, as mentioned

previously, they furnish information on the operating speed of the shutter valves.

As previously described, both the piston meter and the larger secondary reference meter are enclosed so that their temperatures can be regulated by water sprays. When preparing to use the piston meter a sufficient length of time is allowed for the meter temperature to reach that of the spray water before a test is started. As the spray-water temperature is never more than 2 or 3 deg F from the room temperature, it seems reasonable to take the water temperature as the temperature of the meter and the air therein. While no direct comparisons have been made, indirect checks obtained from several calibrations of the secondary reference meter and calculations of the heat-exchanger capacity indicate that the probable uncertainty this may introduce is well under 0.5 deg F.

In the case of the secondary reference meter, the air temperature is measured as it enters and leaves the meter housing, and the mean of these is taken to represent the temperature of the air in the meter. The thermometers used to indicate these two temperatures were interchanged from time to time, which accounts for most of the 0.2 to 0.4 deg differences of temperature observed between these two points. No corrections for calibration or emergent stem were applied to any of the thermometer readings, as such corrections would not modify the final results enough to justify their use.

It is not practical to control the temperatures of the meter under test with a spray system and heat exchanger because of the enormous differences in the sizes of meters involved. This is compensated for as much as possible by operating the industrial meter under steady conditions for a sufficient length of time before the test is started to obtain a practical degree of temperature equilibrium with the air in the room. Also frequent readings of both inlet and outlet temperatures are taken, and the average of the two sets of readings is used as the temperature of the air passing through this meter.

An estimate of the degree to which the deflation of the bag is reproduced may be made from a comparison of the tests of the small secondary reference meter. In three tests of this meter with the piston meter the maximum departure from the average was 0.4 ft^3, while in two comparisons of the meter, operating first in one direction and then the other, the departure from the mean was 0.2 ft^3. As the degree of bag deflation is not the only possible source of variation, it seems probable that the maximum difference in the volumes of air remaining in the bag on successive deflations will not exceed 0.4 ft^3. Since the total volume of air transferred to or from the bag in any test usually exceeds 2,000 ft^3, the 0.4 ft^3 difference in residual volumes represents an uncertainty of only ± 0.02 percent.

(d) Discussion of the sizes and types of meters that can be calibrated

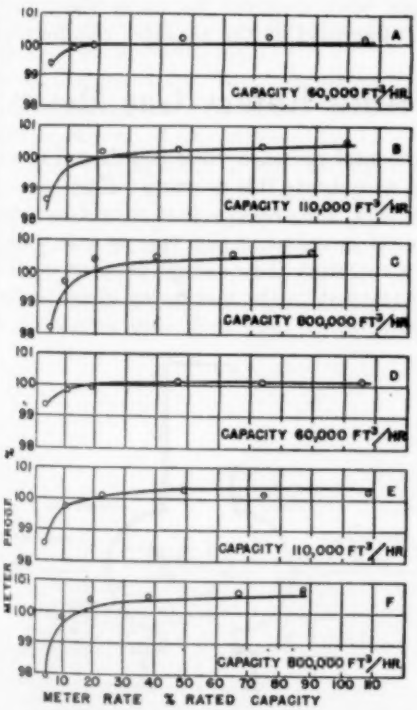
Although this equipment has been used almost exclusively in testing rotary-displacement meters, its usefulness is not limited to such meters. It can be used for testing almost any type of gas meter, such as rotary, bellows, and rate of flow or head, meters, provided the meter can be operated at approximately atmospheric pressure and the pressure drop across the meter will not exceed 9 in. of water. For example, a low differential-pressure orifice meter can be calibrated very readily. In a test of this kind the orifice meter would be connected to the large blower inlet, and the operation of the large shutter valve would be linked to a suitable timing mechanism so that an accurate record would be obtained of the interval of time during which air is discharged into the bag. The total volume of air discharged into the bag would be measured in terms of the bag by the secondary reference meter, and from these data the actual rate of flow through the orifice meter would be calculated.

The range of gas-meter capacities that can be tested is very wide. The upper limit is governed by the capacity of the large blower and the resistance of the ducts to the movement of air through them. The maximum rate obtained thus far was about 700,000 ft^3 of air per hour, and at this rate the operating data, which are not reported, indicated a relatively high pressure drop between the industrial meter and the suction of the large blower. If this flow resistance were reduced by replacing the 23-in. duct with a 30-in. duct, which was the size of the industrial meter connection, a rate approaching 1,000,000 ft^3/hr would be obtained. The lower limit of capacity is not as well defined as the upper one because generally it is not necessary to test meters at rates below 2,000 ft^3/hr, although some tests were made below this figure. If very many tests of

ter are necessary below this figure, it is better connect the meter in series with the piston ter and make a direct calibration. The low-rate ts of the 4- by 12-in. meters reported in section ere made in this way. Also, the small rotary ter, used in the displacement tests of the field thod, was calibrated in this manner, at rates as as 100 ft³/hr.

Comparison of results of testing meters by the two methods

Figures 18, 19, and 20 illustrate the results of ts made by the two test methods on rotary ters ranging in size from a listed displacement pacity of 12,500 to 800,000 ft³/hr. The serv-meter groups represented by these figures are w meters, meters from service of 5 to 15 years both purified and unpurified gas, and a single ter that had been injured by improper clean-. The conditions under which the two test thods were used and the dates differed con-erably. The tests by the transfer method



IGURE 18.—*Results of testing service meters by the two methods, both as received and after cleaning and oiling.*

he solid lines were developed from the results by the field test method while the points are the results by the transfer method.

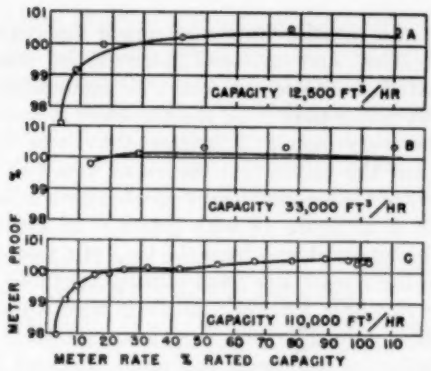


FIGURE 19.—*Results from tests of new meters by the transfer method (points) and the field test method (lines).*

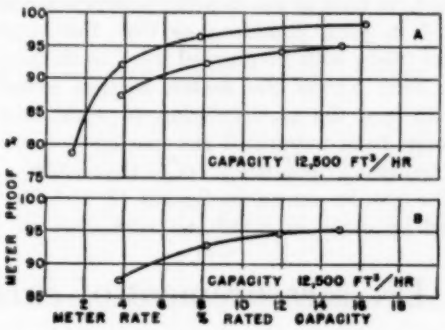


FIGURE 20.—*Results of tests by the two methods of a rotary meter having excessive clearances.*

were made in the shop under closely controlled conditions, whereas the tests by the field method were made under whatever conditions of temperature and weather existed at the time. The time interval between the test by one method and the other was from 1 to 2 years for most of the meters.

In figure 18, the top three graphs show the results of testing the meters as taken from service; the bottom three graphs are the results after the impellers had been cleaned and oiled. By comparing the first with the fourth, and so on, it appears that the cleaning and oiling of the impellers had almost no effect on the value of the meter proofs. However, the spread between the results by the two methods, as represented by the lines and points, is slightly less in the second group than in the first. An explanation for this may be that when making the field tests on meters at their point of service, it was observed that the impellers were covered with a film of oil, whereas

when the transfer tests were made the impellers were drier, and material removed in cleaning appeared to be such as would be accumulated in transit rather than from the gas while in service.

The very small difference that was found between the calibration curves of new and used meters of the same size is illustrated by comparing graph *E* of figure 18 with graph *C* of figure 19. The latter graph was from the tests of a new meter while the former was from a meter that had been in service over 5 years. As there were a number of other cases like this, it appears probable that the effect of age upon the proof curve of these meters is almost negligible, at least within the age limit of meters tested (about 20 years). Indeed, so long as the impeller bearings are maintained in good condition so that the impellers rotate freely with no marked increase in the pressure drop across the meter, neither length of service nor the accumulation of scale and tar deposits from unpurified gas seemed to have any marked effect upon the proof of the meters.

The graphs shown in figures 18 and 19 were based on tests in which air was used in both methods of calibration. In order to illustrate an exaggerated manner the differences betw meter-proof curves for air and fuel gas, as m tioned in connection with the field method cl ance tests, tests were made upon a meter in wh the clearances had been increased far beyond th which could be accepted in an industrial me The results of these tests are shown in figure In both graphs the lines represent the res obtained by the field method, and the circles the individual tests by the transfer meth The upper curve and test points in *A* illustra the direct comparison of the two test meth when the meter was calibrated with air. T lower curve and test points in *A* illustrate direct comparison of the two test methods wh the meter was calibrated with fuel gas. In the circles are the results by the transfer meth when using fuel gas. The curve was deri from the field method when the clearance test w made with air, and the values of both clearan flow and meter proof to be expected when meter fuel gas were obtained by using the conver factors provided by the auxiliary clearance test

IV. Measurement of Pressures Within Rotary Gas Meters

1. Instantaneous pressures within the closed measuring pockets of a rotary meter

The rate of discharge from a rotary gas meter, operating at a constant pressure and speed, fluctuates slightly. These fluctuations have a highly distorted sine wave shape with maximum and minimum rates, respectively, about 1.75 percent above and below the average rate. Four complete wave cycles occur with each revolution of the meter. The momentum of the rotating impellers opposes any shift in their rotating speed, while the momentum of the gas flowing through the meter and adjacent piping opposes any shift in the flow rate through the meter. The result of these two opposing forces causes pressure waves, or surges, to be set up in the inlet and outlet connections of the meter. This condition may cause slight irregularities in the proof of a rotary meter by imposing on the gas, as the metering chambers close, momentary pressures that are higher or lower than the average inlet static pressure. Also, the arrangement of the inlet piping and the meter speed may be such that a portion of the fundamental pressure wave is reflected in a m ner to accentuate this pressure difference.

Actually, the pressure that should be measu and used in reducing the volume indicated b rotary meter is the average pressure of the while trapped in the measuring chambers dur the interval of time each compartment is co

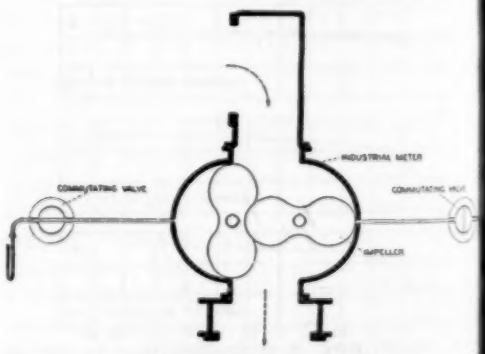


FIGURE 21.—*Diagrammatic representation of method measuring the instantaneous pressure within a cl metering chamber.*

The cores of the commutating valves were gear driven from the impe shafts at twice the impeller speed.

ely closed. In order to measure this pressure, special commutating valves were built. se valves were driven by the meter through a r train at twice the meter speed, and were so chronized with the impellers as to be open during the interval each respective chamber completely closed. Inclined water manome- were used to measure the pressures, and nections from the meter chambers through the ves to the gages were made as short as possible. se connections are shown diagramatically in re 21, and figure 22 shows two sectional ws of the valves.

Using these commutating valves, a meter was ed by the transfer method with various inlet ng arrangements. These piping arrangements e chosen to create exaggerated pulsating con- ons at the inlet of the meter by the reflection pressure waves from the open end of various gths of pipe attached to the meter inlet. The s of meter operation were selected to include se at which maximum differences were ob- ed between the average static pressure at meter inlet and the instantaneous pressures in the metering chambers.

The conclusions drawn from this series of tests, h are summarized in table 4, are: First, with pipe connected to the meter inlet (i. e., the mal test arrangement), the average static sure, as measured at the regular inlet pressure , is a satisfactory pressure value for use in puting the meter proof and introduces no reciable error. Second, regardless of the t piping arrangement and its resonant char-

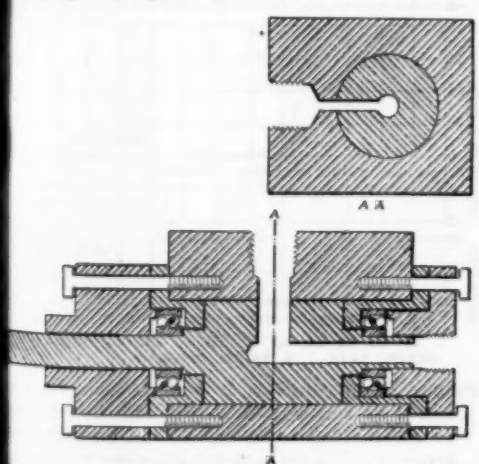


FIGURE 22.—*Cross sections of the commutating valves.*

acteristics, the use of the instantaneous static pressure within the meter chambers while closed will practically eliminate the effects of pulsation. Third, the magnitude of the effects of reflected pulsations obtained with two different lengths of inlet pipe were practically the same and were relatively small, the maximum being about 0.6 percent.

TABLE 4.—*Effects of pulsations in the meter inlet upon the proof of a 6- by 18-in. rotary meter*

Test number	Date	Pressures			Meter proof		Meter speed, percentage of rated capacity
		Differential across meter	Average inlet	Closed measuring pockets	Average inlet pressure	Closed measuring pockets	
1	2	3	4	5	6	7	8
A—ONE 8-IN. ELBOW AND 16 FT. OF 8-IN. PIPE CONNECTED TO METER INLET							
		in. H_2O	*in.* H_2O	*in.* H_2O	%	%	%
612	6-4-40	0.408	−0.04	+0.213	99.67	99.74	25.49
611	6-3-40	.542	−.11	+.456	99.91	100.06	40.81
610	6-3-40	.774	−.25	−.204	100.21	100.19	60.81
609	6-3-40	1.37	−.69	+1.61	99.92	100.49	99.92
608	6-3-40	1.55	−.75	+.150	100.22	100.44	103.57
607	5-29-40	1.52	−1.19	−2.20	100.65	100.42	131.28
606	5-29-40	1.86	−1.48	−1.77	100.45	100.41	144.17
B—ONE 8-IN. ELBOW AND 8 FT. OF 8-IN. PIPE CONNECTED TO METER INLET							
605	5-29-40	0.429	−0.09	+0.163	99.70	99.76	26.78
604	5-29-40	.618	−.11	+.340	99.85	99.96	40.02
603	5-28-40	.830	−.20	+2.21	99.60	100.20	54.67
602	5-28-40	.891	−.27	+.276	100.08	100.21	63.63
600	5-28-40	1.39	−.77	−1.70	100.52	100.29	106.70
626	6-7-40	1.37	−.74	−1.63	100.60	100.38	107.03
601	5-28-40	1.74	−1.37	−1.26	100.35	100.37	141.77
C—NORMAL INLET ARRANGEMENT—NO PIPE ON METER INLET							
620	6-6-40	0.390	−0.02	−0.071	99.90	99.90	26.32
621	6-6-40	.818	−.06	−.144	100.13	100.16	40.03
622	6-6-40	.725	−.15	−.226	100.27	100.25	59.90
623	6-6-40	1.21	−.45	−.734	100.49	100.42	99.97
624	6-6-40	1.49	−.77	+.32	100.30	100.57	132.33
625	6-6-40	1.69	−.94	−1.23	100.49	100.40	149.49

It should be kept in mind that the pulsations discussed here are those which originate from the action of the meter itself, and not from an outside source. Also, the open-end pipes produce the maximum reflection that is to be obtained.

2. Instantaneous pressure at the inlet pressure tap of a rotary meter

The tests described above gave rise to the suggestion that at some angle of the impellers the

instantaneous pressure, measured at the regular inlet pressure tap of the meter, would agree very closely with the instantaneous pressures within the closed metering chambers, regardless of the meter rate or the resonant characteristic of the inlet piping. To test this, the inlet pressure tap of the meter was connected to an inclined manometer through another commutating valve. The commutating element of this valve was a disk having four holes near the periphery and 90° apart. This disk rotated over the inlet port of the valve and was coupled directly to one of the meter impeller shafts. The azimuth of the disk on its shaft could be changed rapidly and easily, without interrupting the operation of the meter, so that the open position of the valve could be made to occur at different phase angles of the impellers.

In this group of tests the meter was run at different speeds throughout its operating range. At each speed measurements of the instantaneous static pressure at the regular inlet pressure tap were made for nine angular positions of the impellers. In the first of these the valve was fully open when one impeller was vertical. The setting of the disk was changed between each group of readings by steps of 3.75° so that on the ni setting when the valve was fully open the imp had dropped back to 30° from vertical. At same time, readings were made of the aver static pressure at the inlet tap, and of the stantaneous static pressure in the closed mete chamber. In this manner three sets of pres surveys were made using the inlet piping arra ment listed in table 4.

Plots of the instantaneous inlet pressures three of the nine angular positions of the impe are shown in figure 23. The graphs *A*, *B*, an refer respectively to the three inlet piping arra ments. The zero line in each graph repres the average inlet pressure as measured by regular pressure tap and gage.

A comparison of these pressure lines, for nine positions of the impellers, with the line o closed chamber pressure showed that when impeller is 7.5° in advance of the vertical the stantaneous inlet pressure corresponds very clo with the closed chamber pressures. Figure shows plots of these two pressures for the t inlet arrangements. In considering the result these instantaneous pressure measurements, illustrated by figures 23 and 24, it should be n

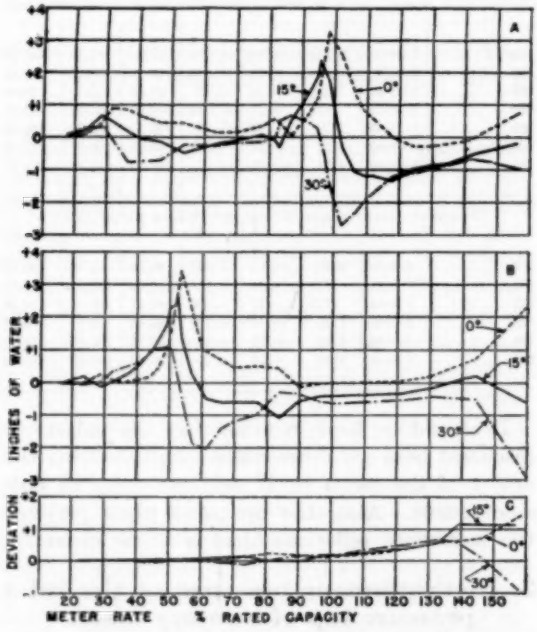


FIGURE 23.—*Variations of the instantaneous static pressure at the regular inlet-pressure tap for three phase angles of the impellers and three inlet-piping arrangements.*

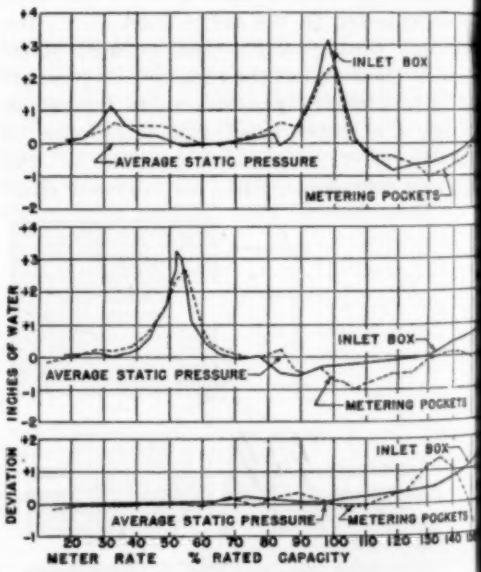


FIGURE 24.—*Comparison of the instantaneous static p sure at the regular inlet pressure tap when the impe are 7½° ahead of the close-off, with the instantaneous pressure within the metering chambers when closed, three inlet-piping arrangements.*

a variation in the static pressure of 2 in. of
er will affect the meter proof by 0.5 percent.
ce, the maximum effect from pulsations, which
d be produced in these tests, would amount
bout 0.8 percent in the proof of the meter.
reover, these maximum effects occurred over
ry narrow range of meter rates. Over the
or portion of the operating range of the meter
difference between the average inlet pressure
either the instantaneous inlet pressure, or the
sure in the closed metering chamber is too
ll to have any significant effect on the meter
f. This is especially so for the open-inlet
lition, graph *C*, as normally used in testing
e meters.

lthough pressure waves are generated by the
on of these meters, the very small spread of
lines in graphs *C* indicate that these pressure
es do not directly affect the closed metering
mber pressure, or, therefore, the proof of the
er. The only effect from these pressure waves
rred when they were reflected by the inlet pipe
ch a frequency as to enter the metering cham-
when the impeller was 7.5° from the close-off
tion. This is a function of the meter speed and the resonance of the inlet piping, not of the meter.

As the open-end pipes used in these tests reflected pressure waves move effectively than will the usual closed piping system on the inlet of an installed meter, it is probable that the effects of reflected pulsations in any actual meter installation will be very much less than shown by these tests. Also, for pulsations from any outside source to have any effect upon the meter, it will be necessary for their frequency and phase to be such that they reach the metering chambers as the impellers are 7.5° from the close-off position. Such a condition seems remote indeed. However, if the question arises in connection with an actual meter as to whether pulsations from any source are affecting the inlet pressure measurement or the measuring chamber pressure, a survey can be made of the instantaneous pressures at the inlet pressure tap by the use of a commutating valve. From the results thus obtained the magnitude of any pulsation effects may be determined and a method of taking account of them agreed upon.

WASHINGTON, August 8, 1945.

MATHEMATICAL TABLES

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Attention is invited to a series of publications prepared by the *Project for the Computation of Mathematical Tables* conducted by the Federal Works Agency, Work Projects Administration for the City of New York, under the sponsorship of the National Bureau of Standards. The tables which have been made available through the National Bureau of Standards are listed below. A list of other WPA tables obtainable elsewhere will be sent by the Bureau on request. There is included in this list a publication of the hypergeometric and Legendre functions (MT15), prepared by the Bureau.

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1.0000 to 2.5000	.0001	15
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